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Rosenflanz

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(54) **FUSED Al_2O_3 -RARE EARTH OXIDE-ZRO₂ EUTECTIC MATERIALS**

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(52) **U.S. Cl.** **51/309**; 51/307; 501/105; 501/126; 501/127; 501/152; 501/153; 264/332

(58) **Field of Search** 51/307, 309, 295; 501/126, 127, 152, 153, 105, 104; 264/332; 423/593, 600, 608

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(57) **ABSTRACT**

Fused, crystalline eutectic material comprising Al_2O_3 -rare earth oxide-ZrO₂ eutectic. Examples of useful articles comprising the fused eutectic material include fibers and abrasive particles.

32 Claims, 16 Drawing Sheets

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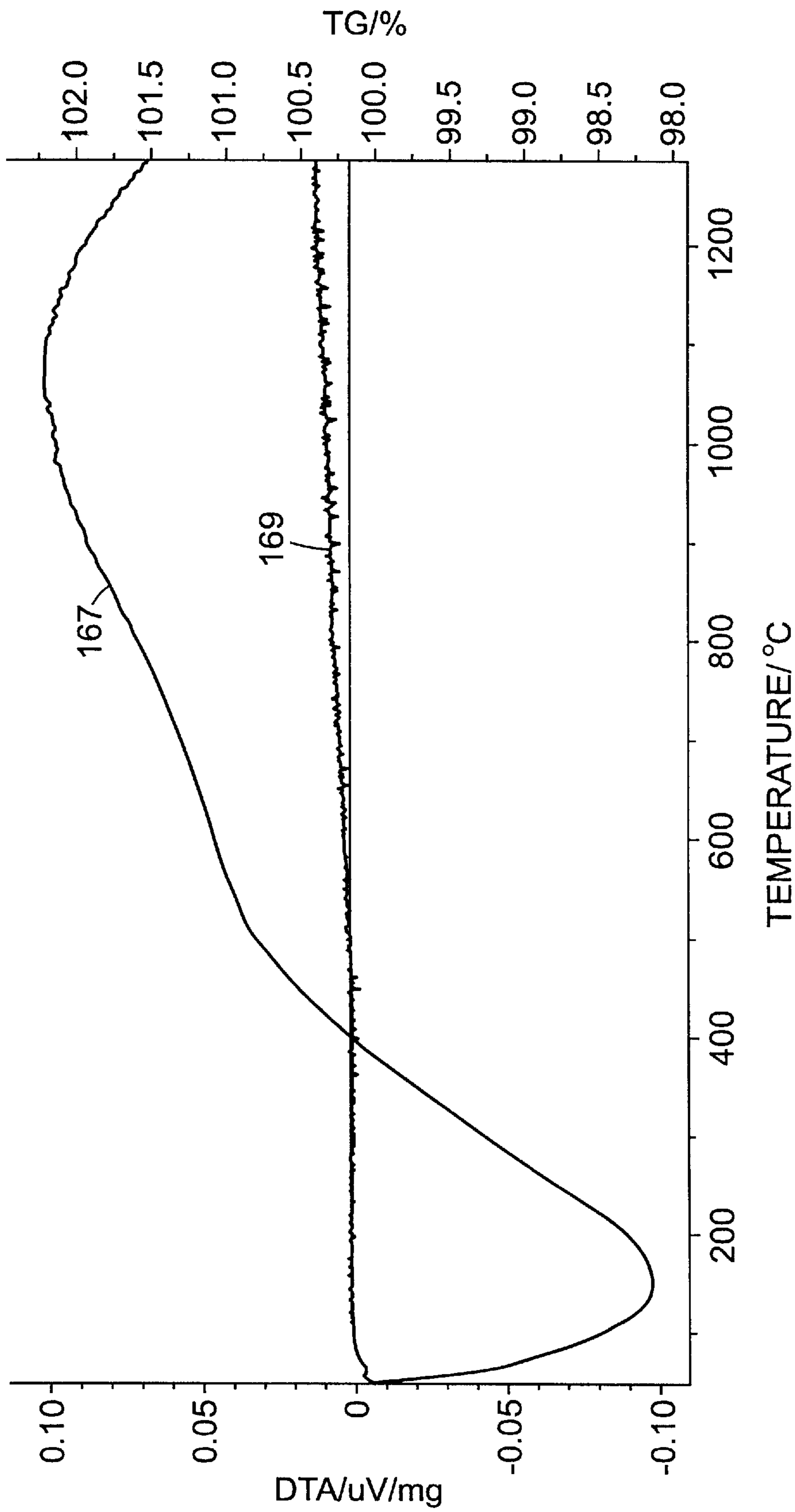


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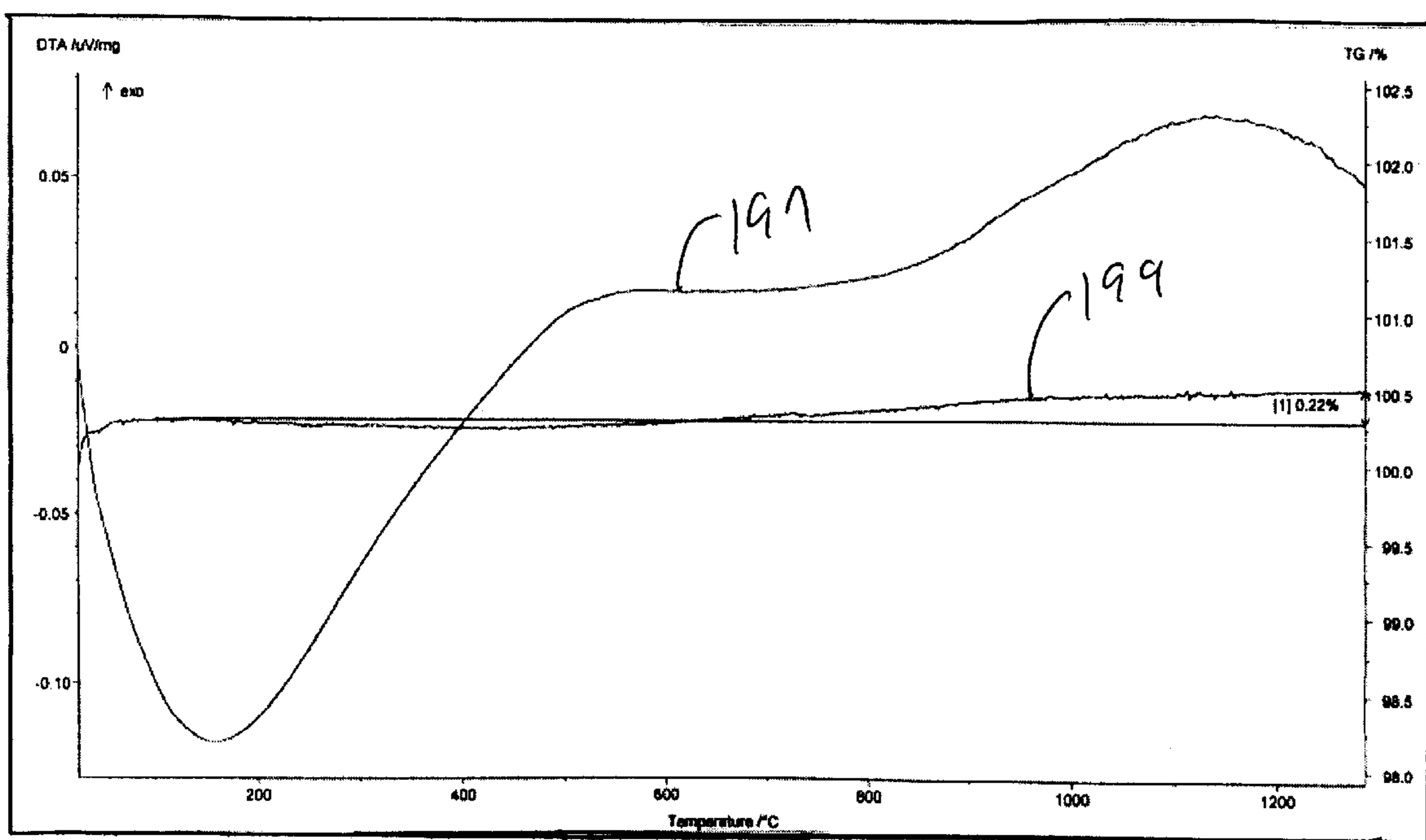


Fig. 2

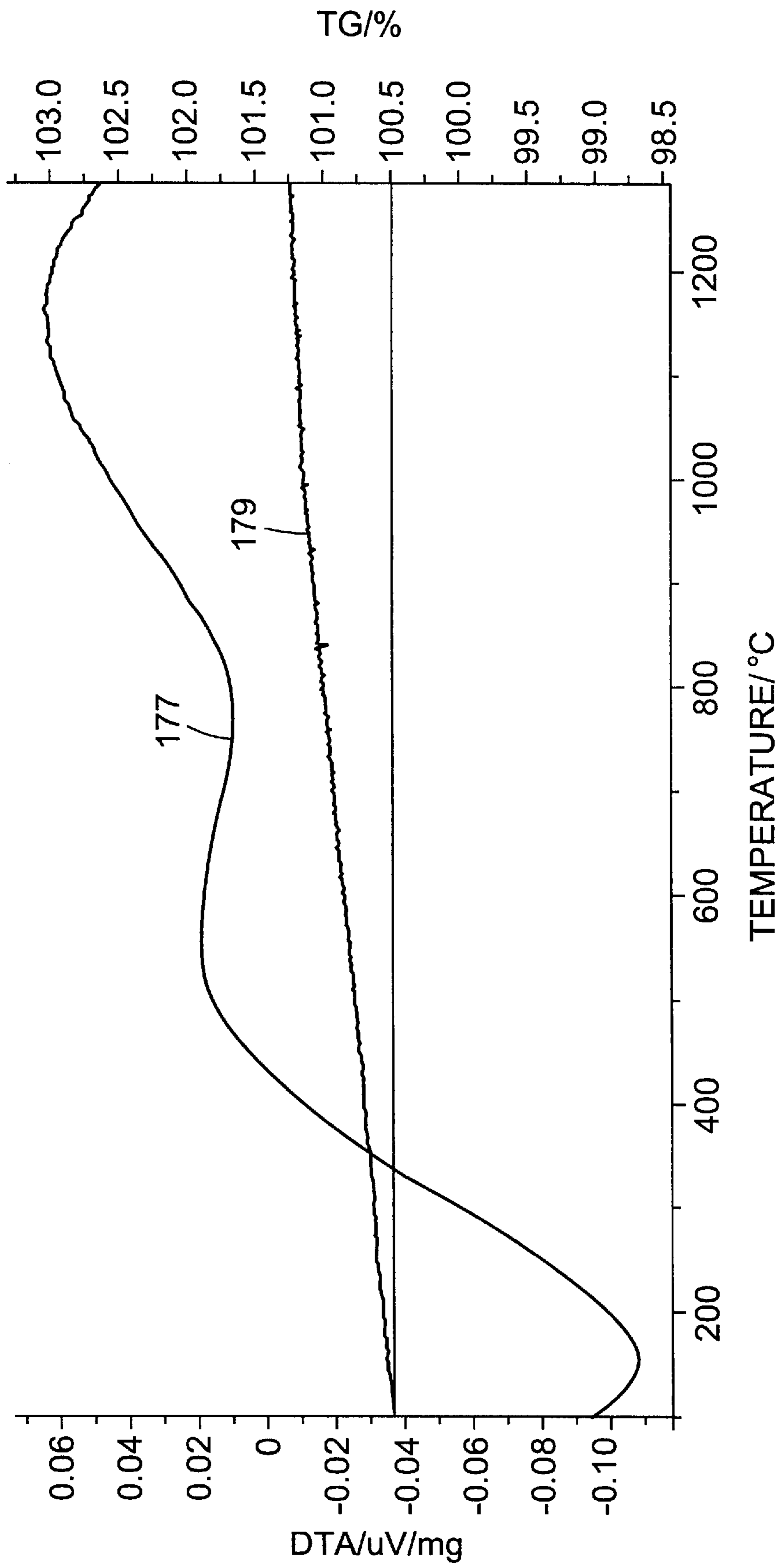


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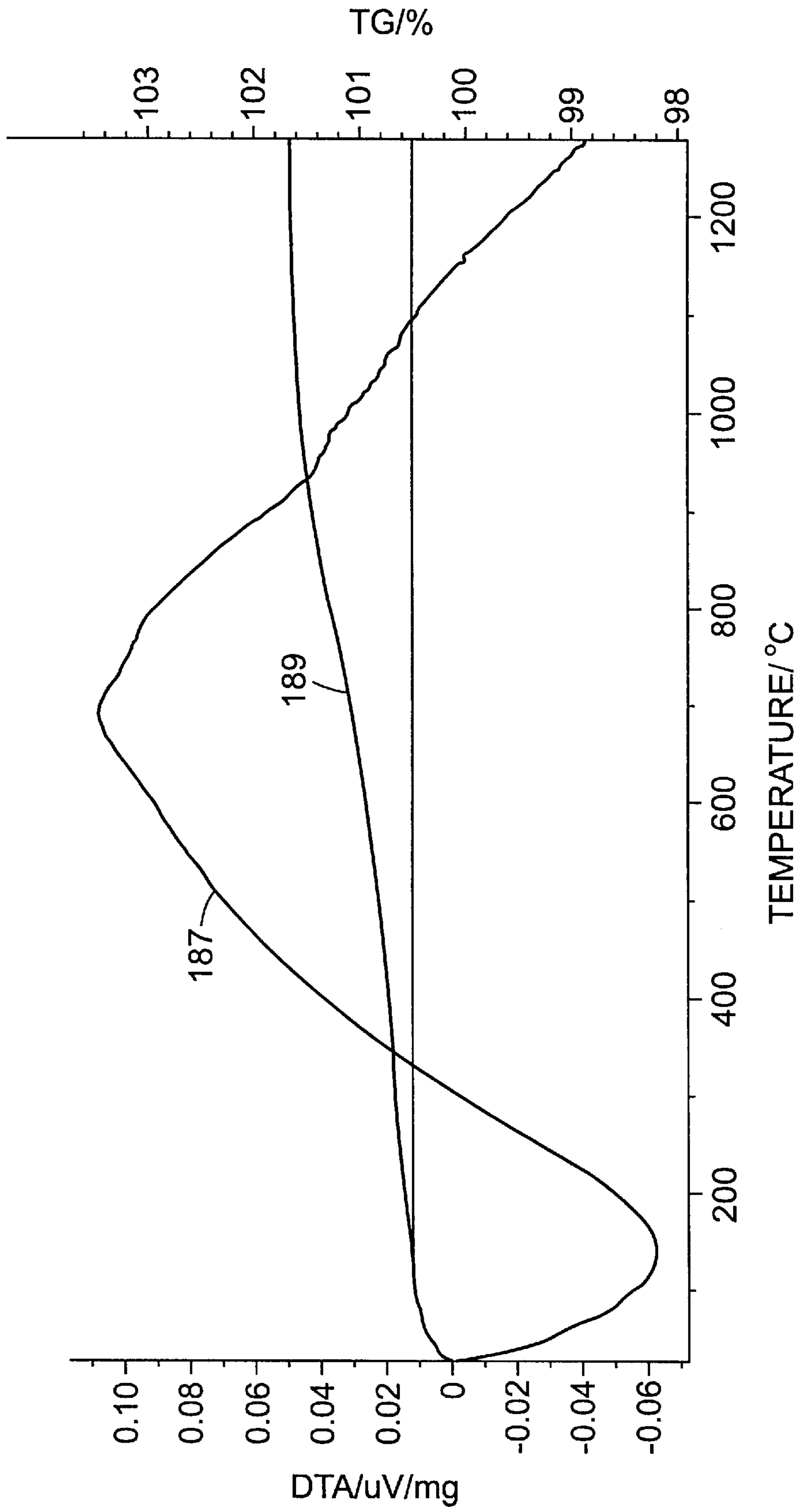


Fig. 4

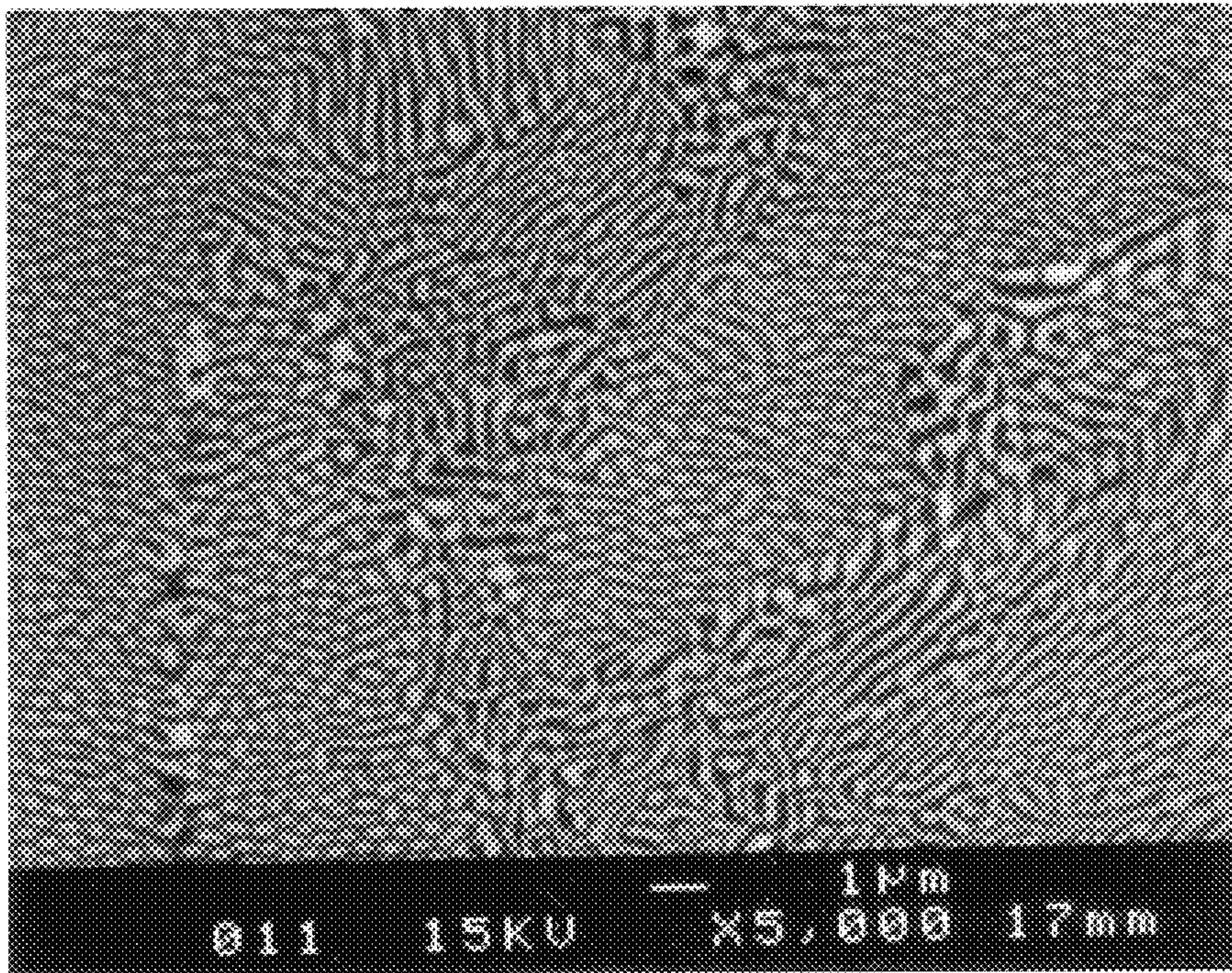


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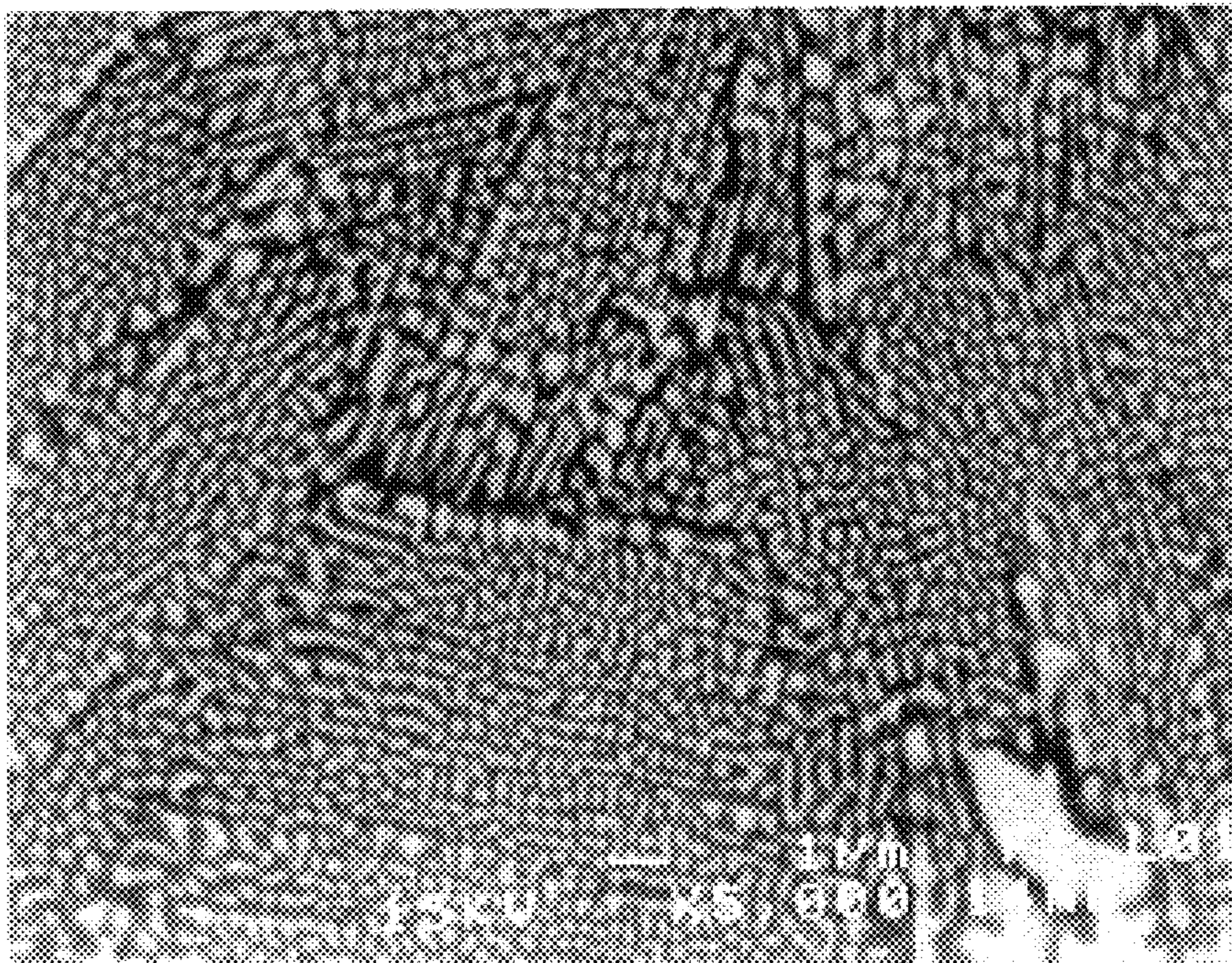


Fig. 6

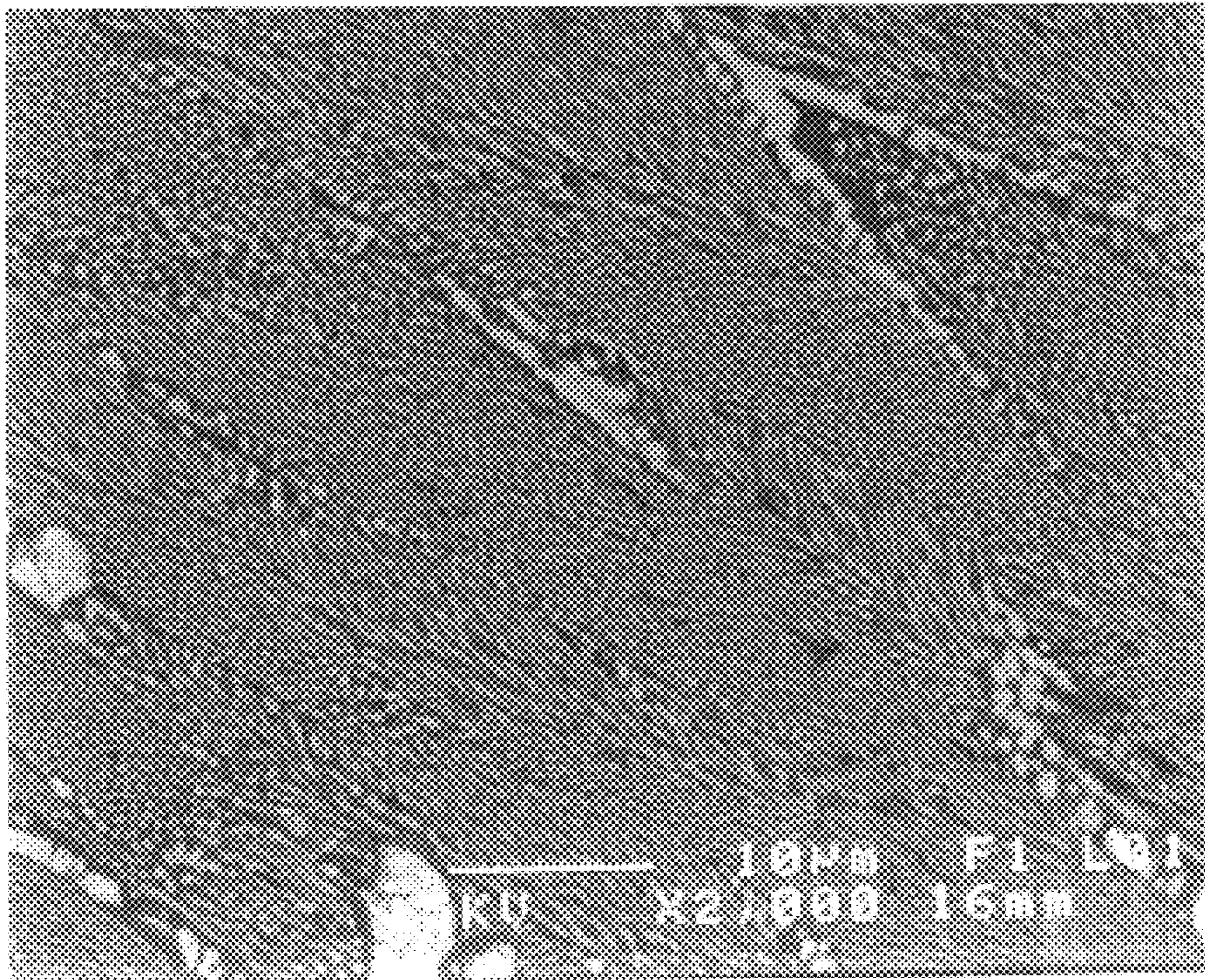


Fig. 7

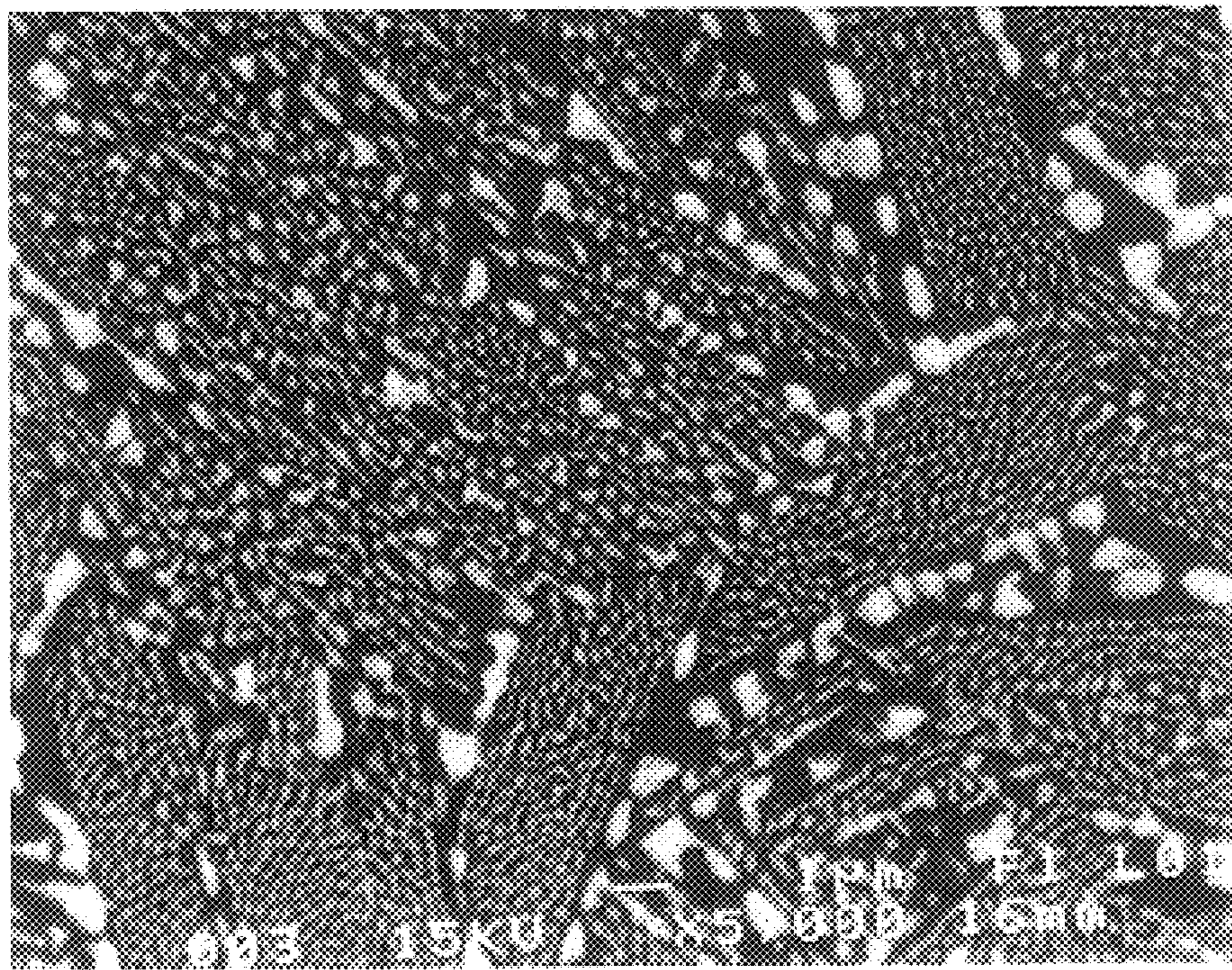


Fig. 8

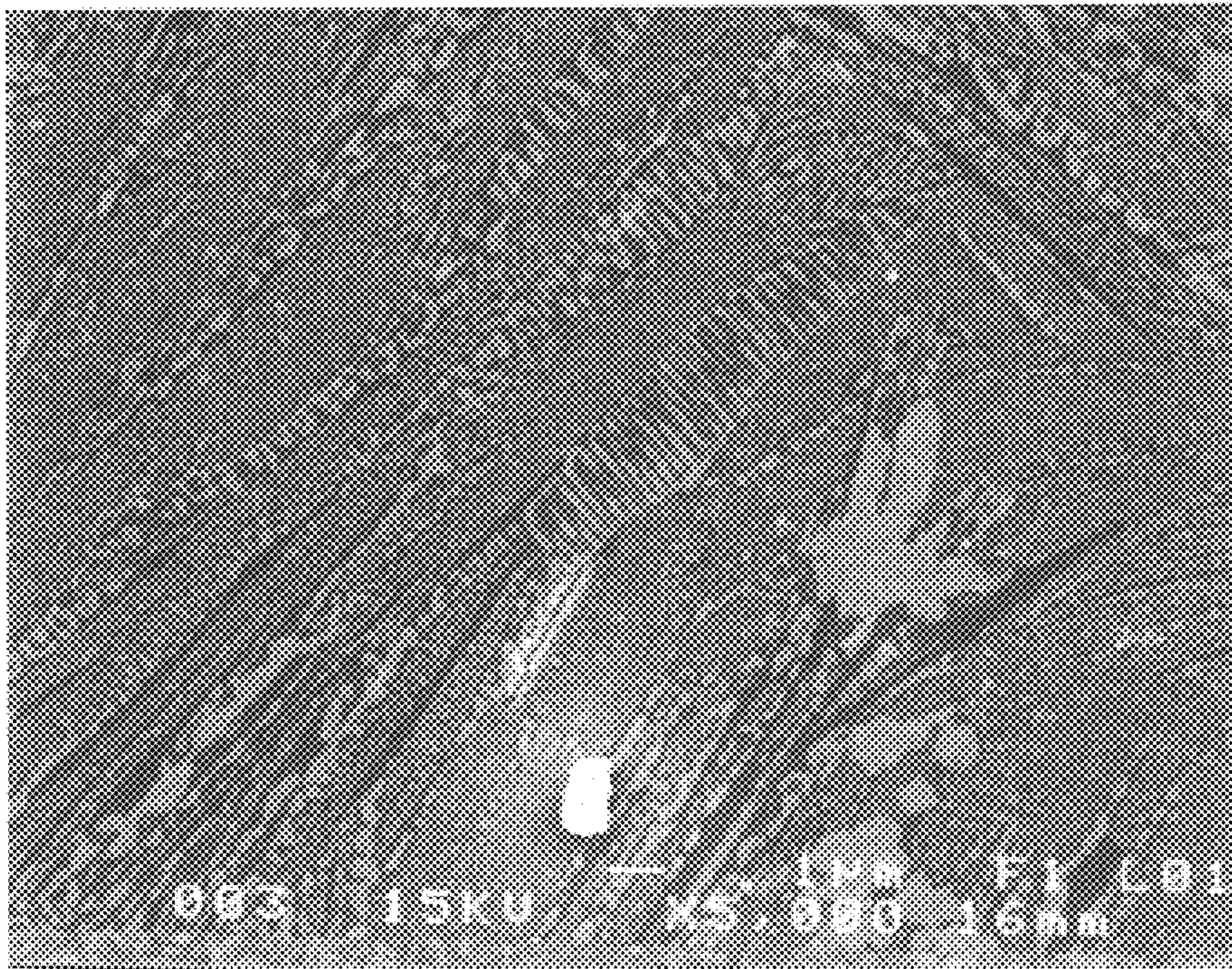


Fig. 9

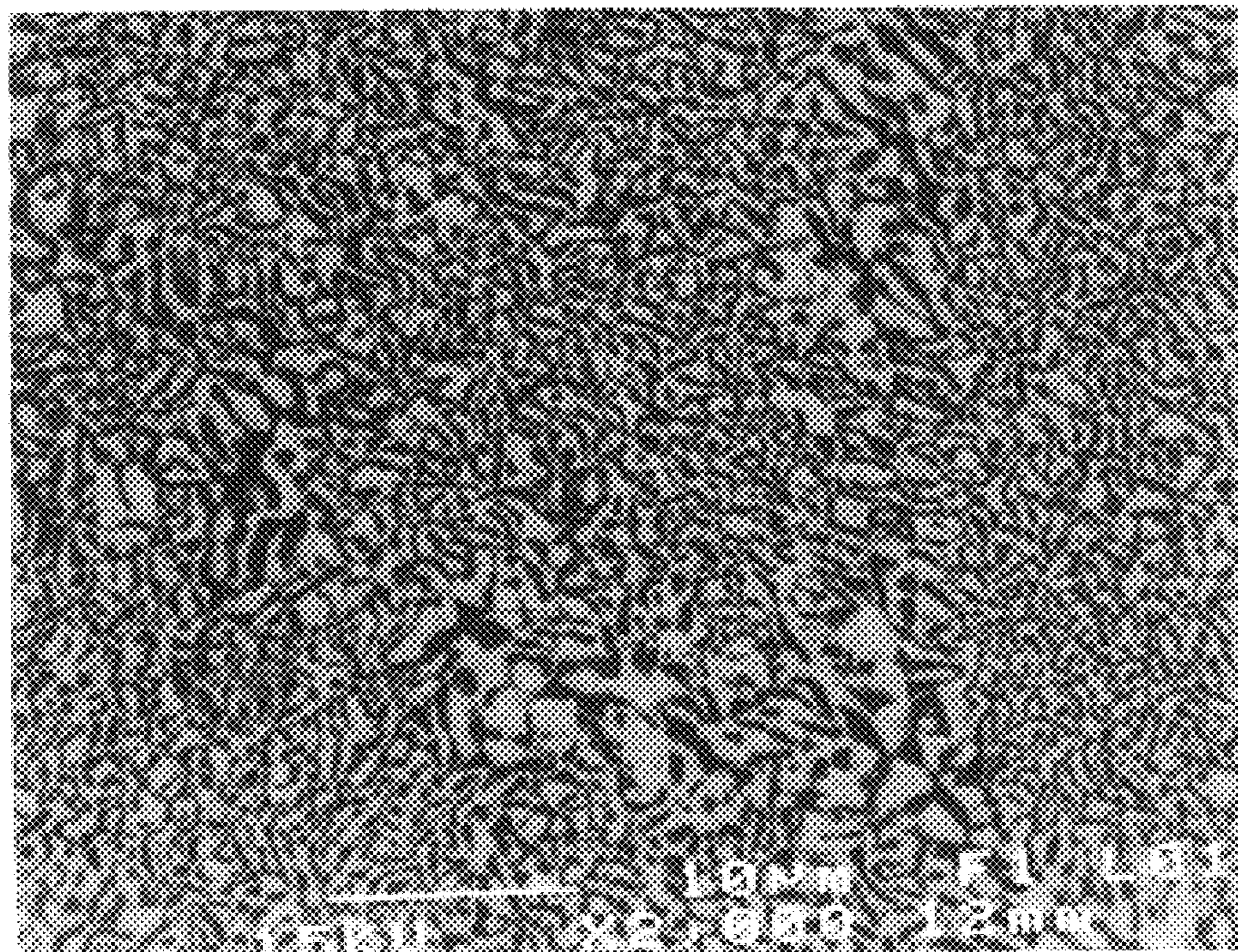


Fig. 10

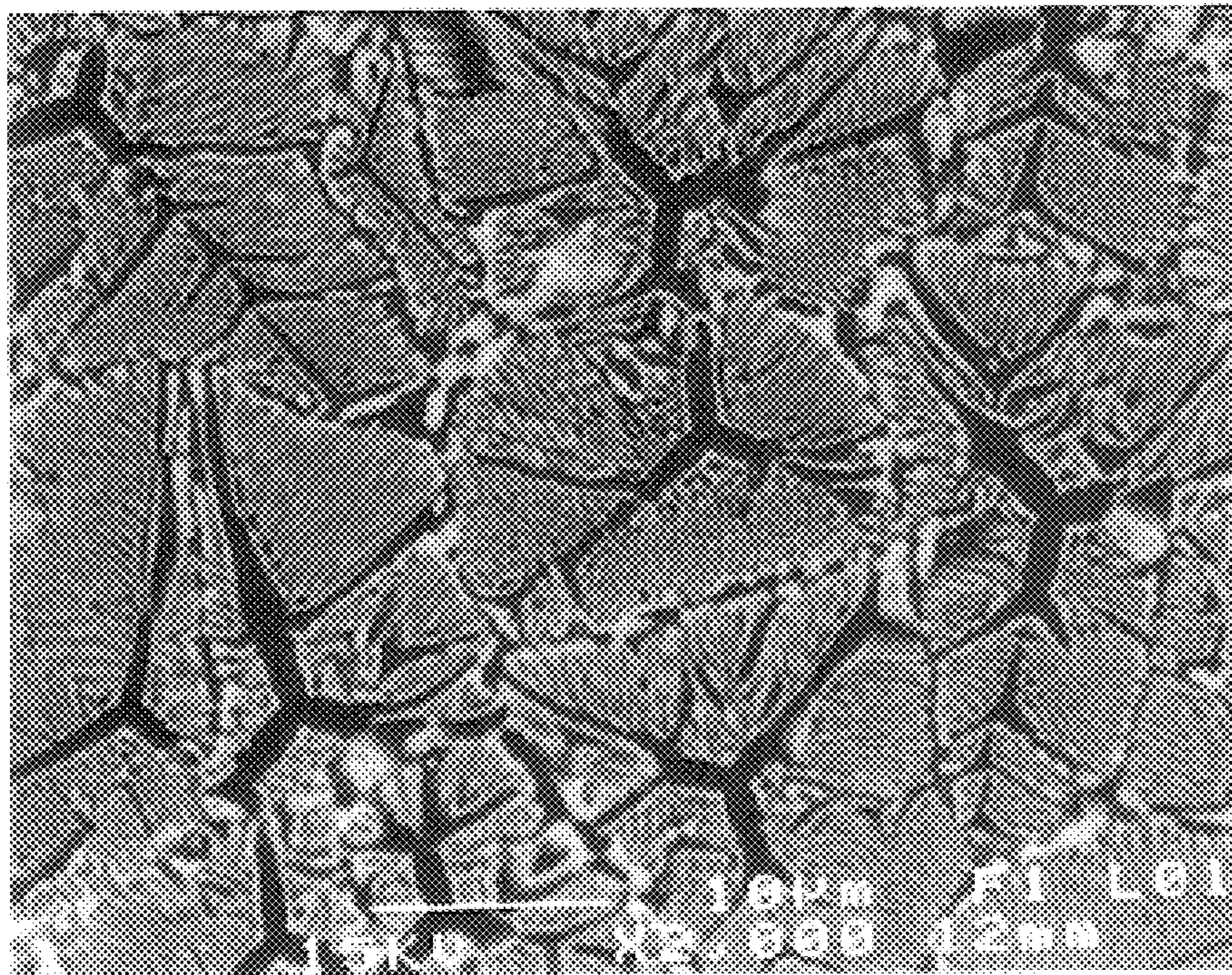


Fig. 11

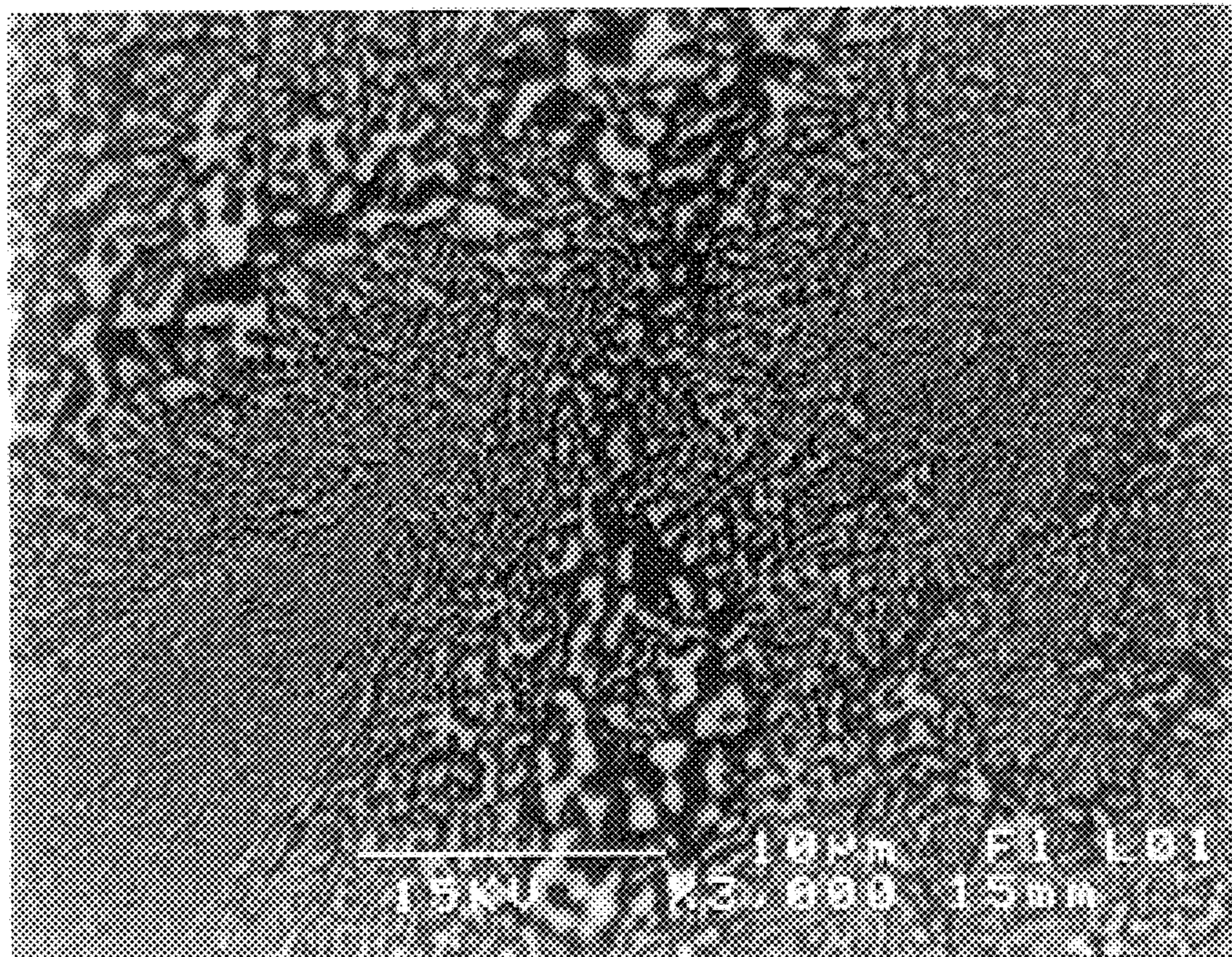


Fig. 12

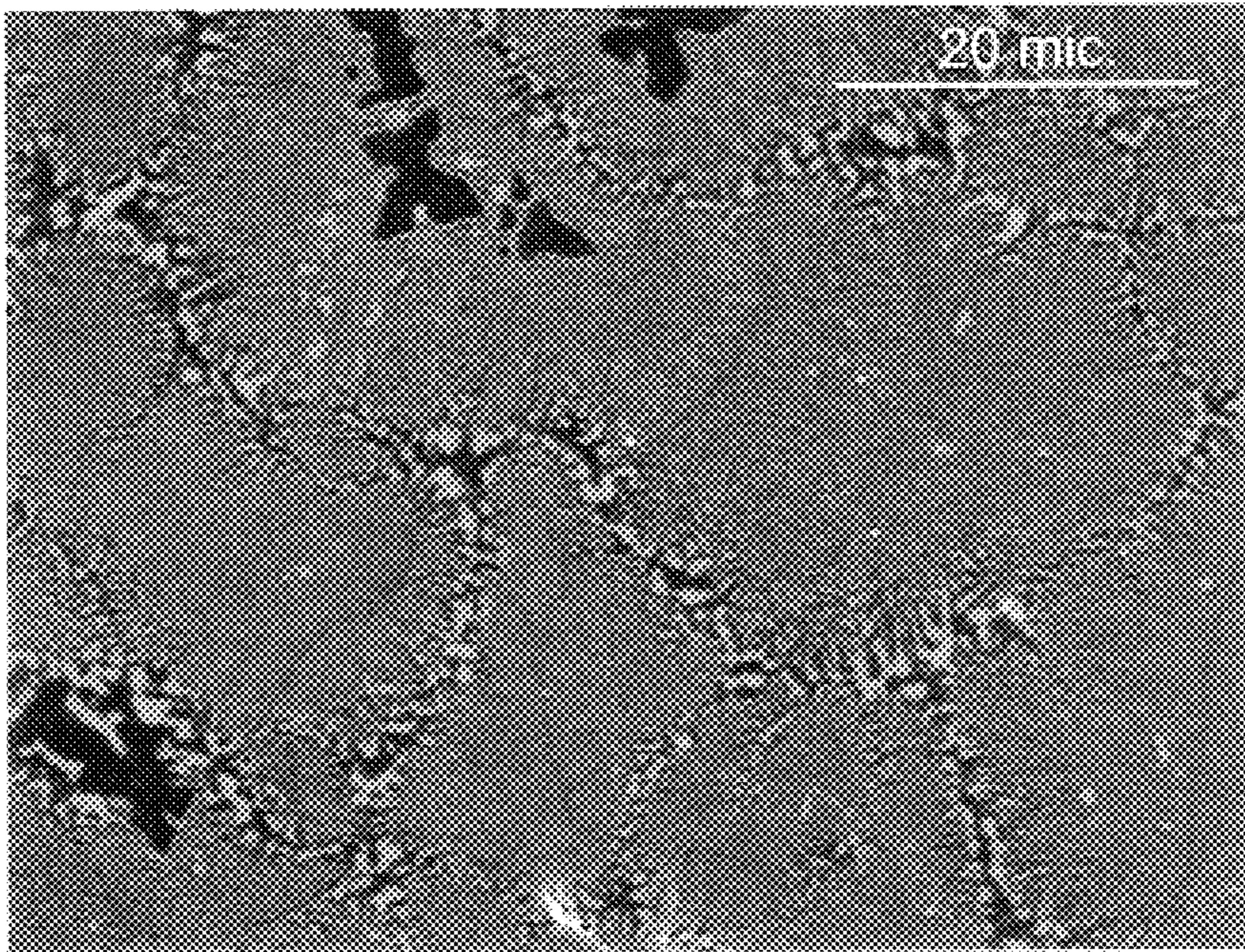


Fig. 13

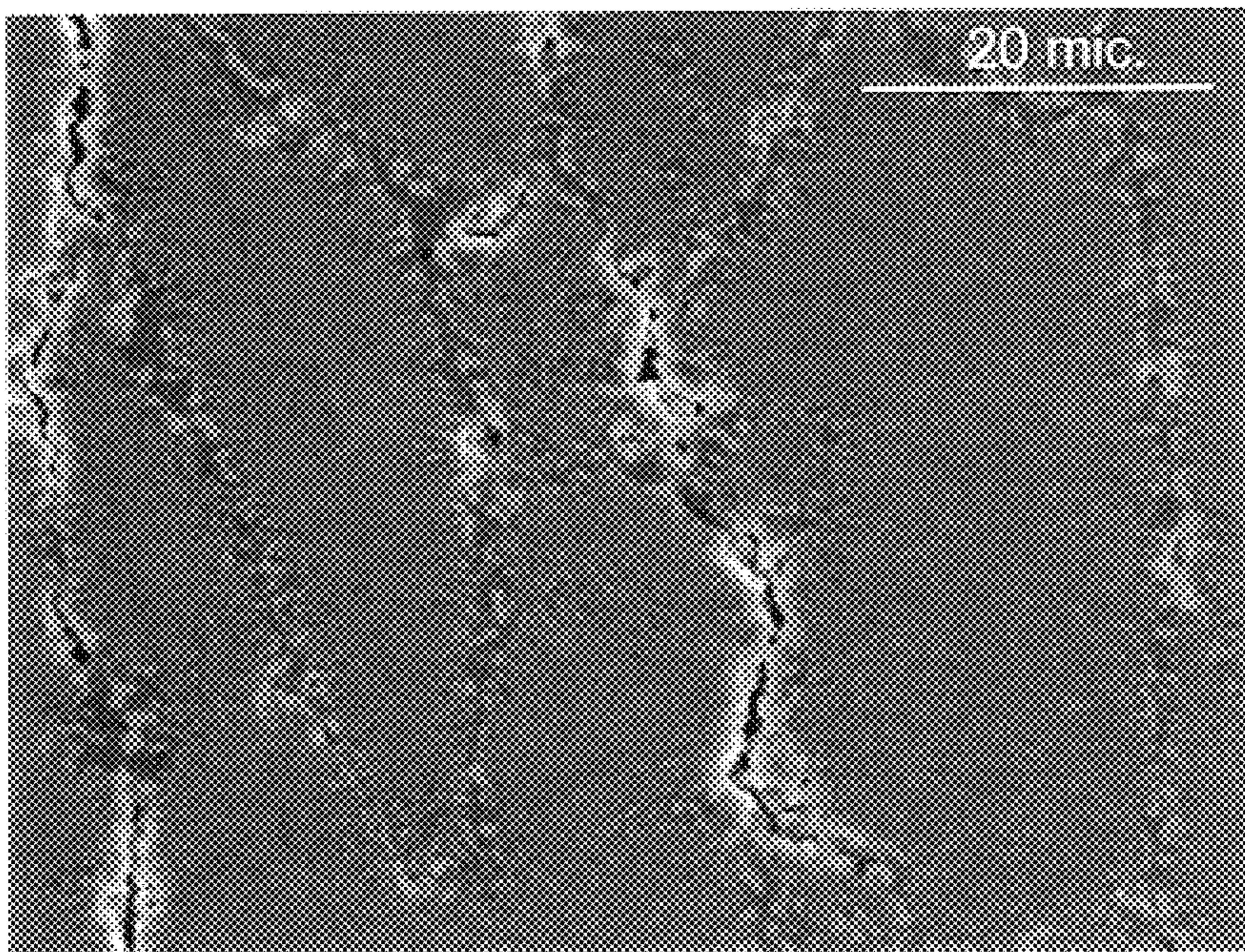


Fig. 14

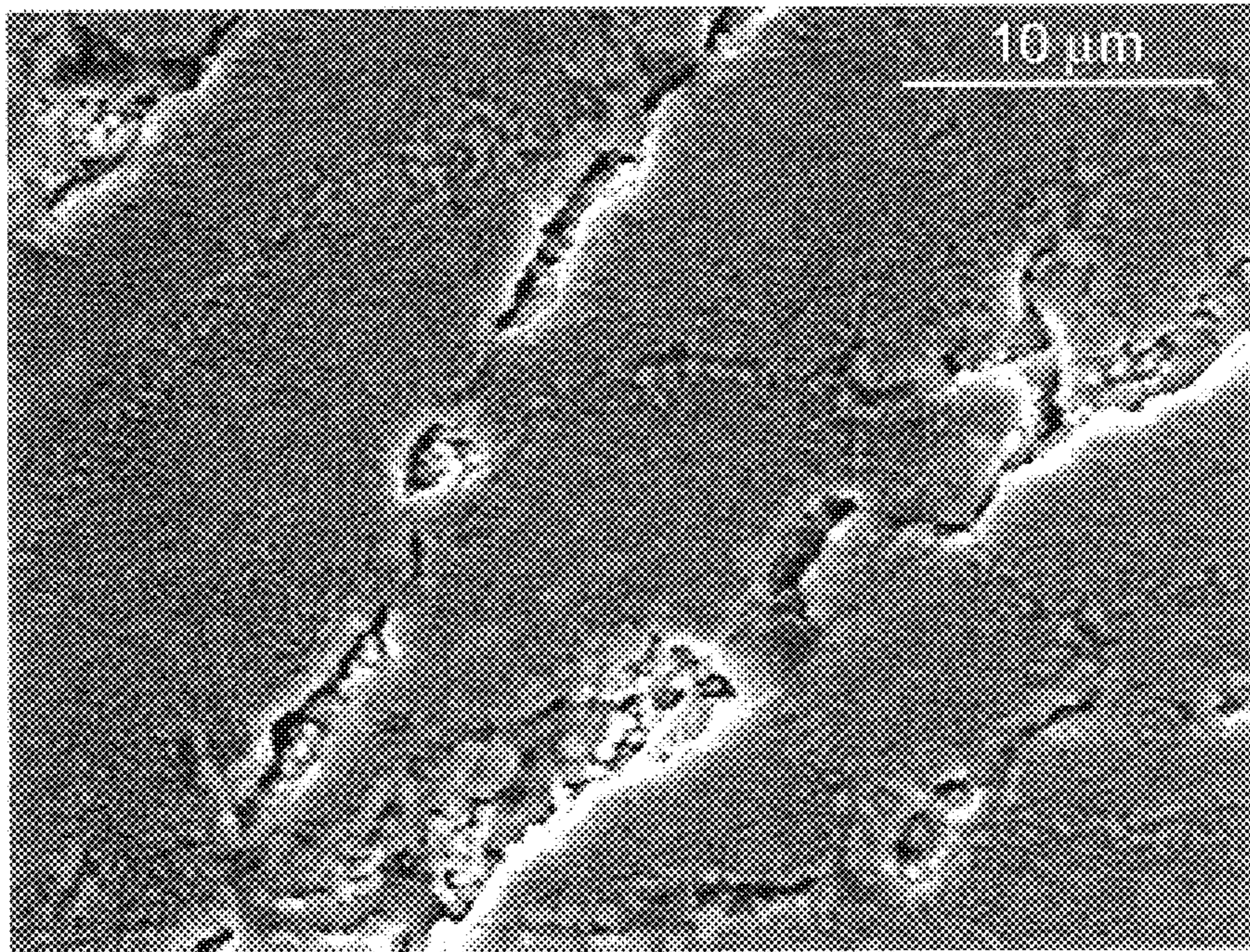


Fig. 15

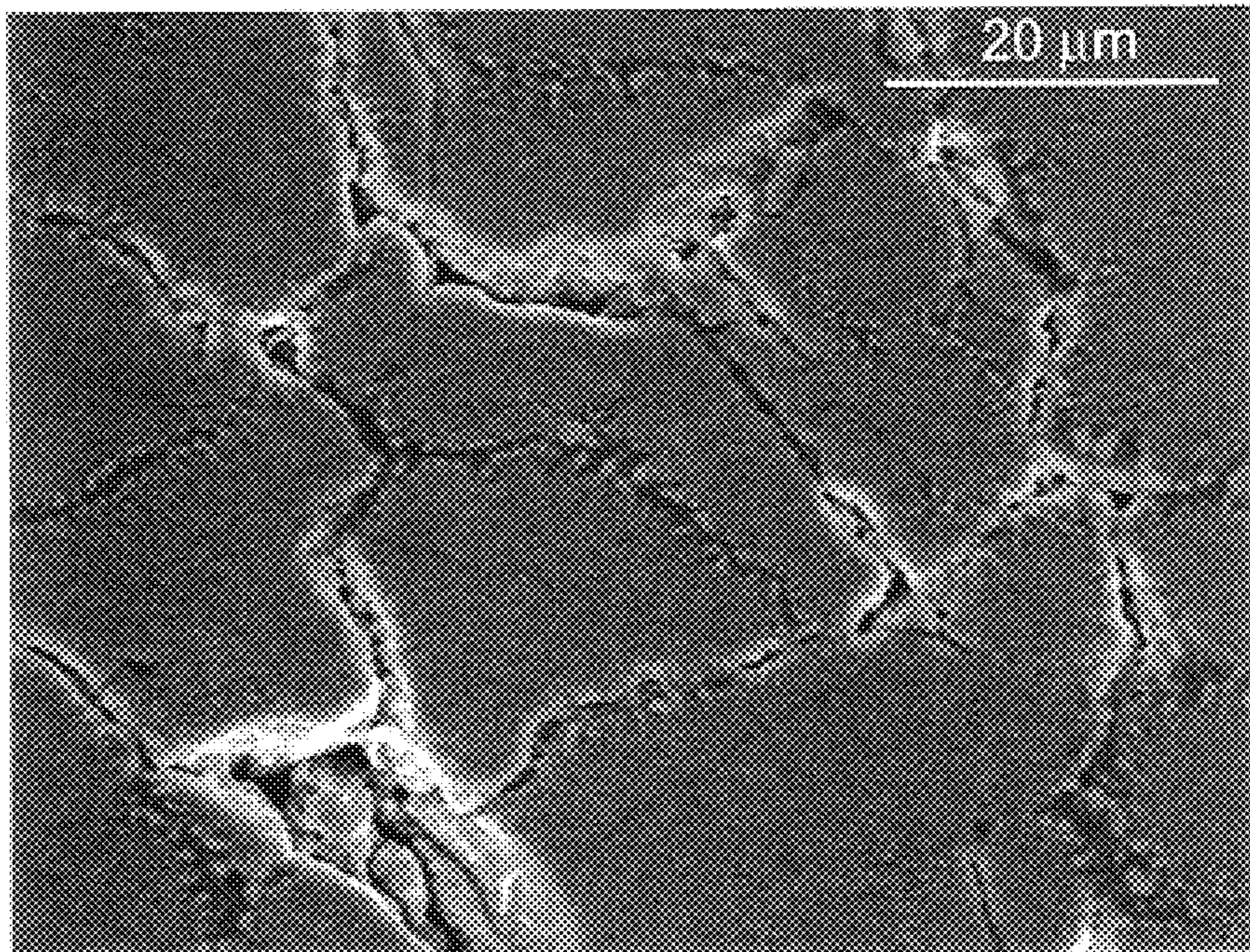


Fig. 16

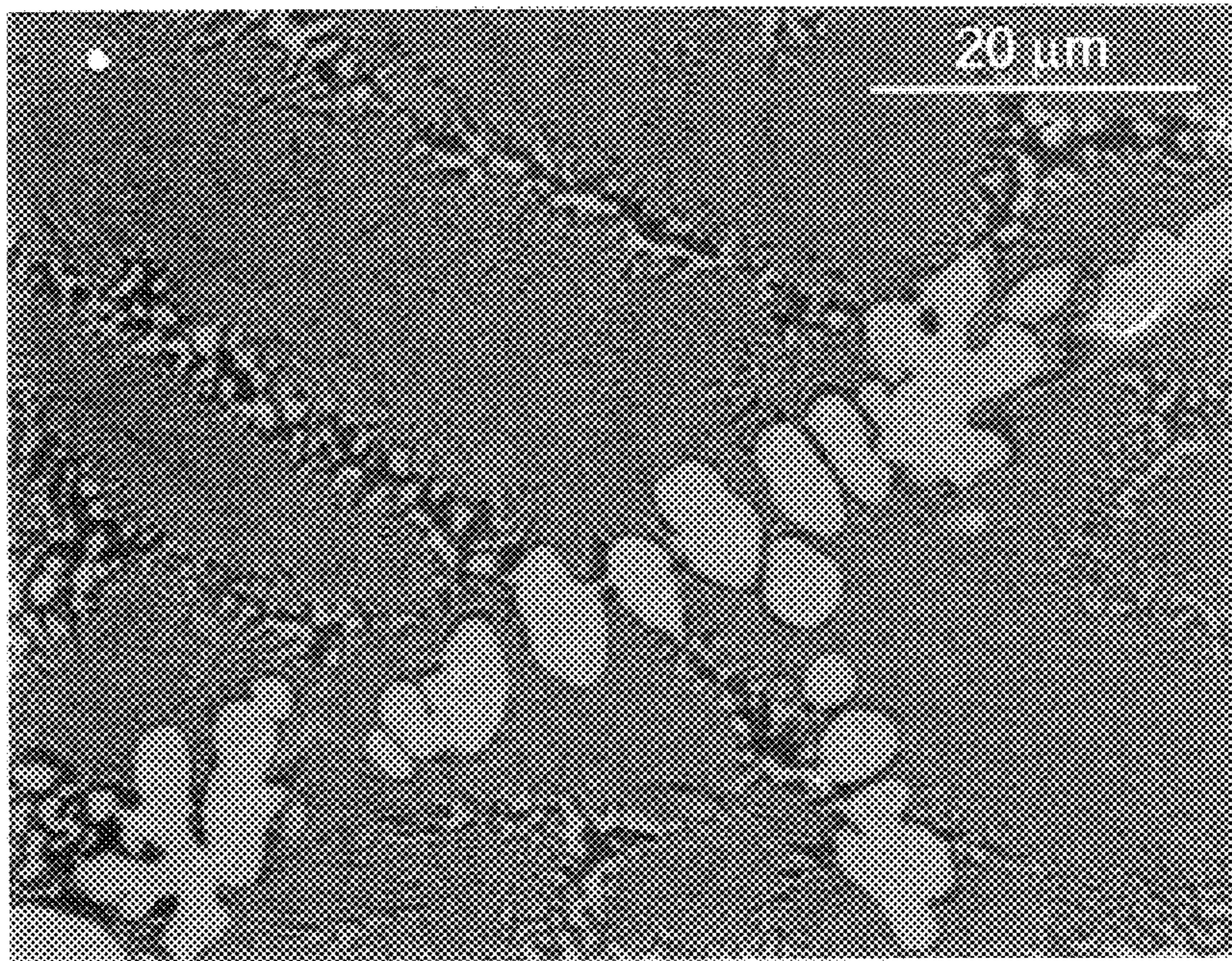


Fig. 17

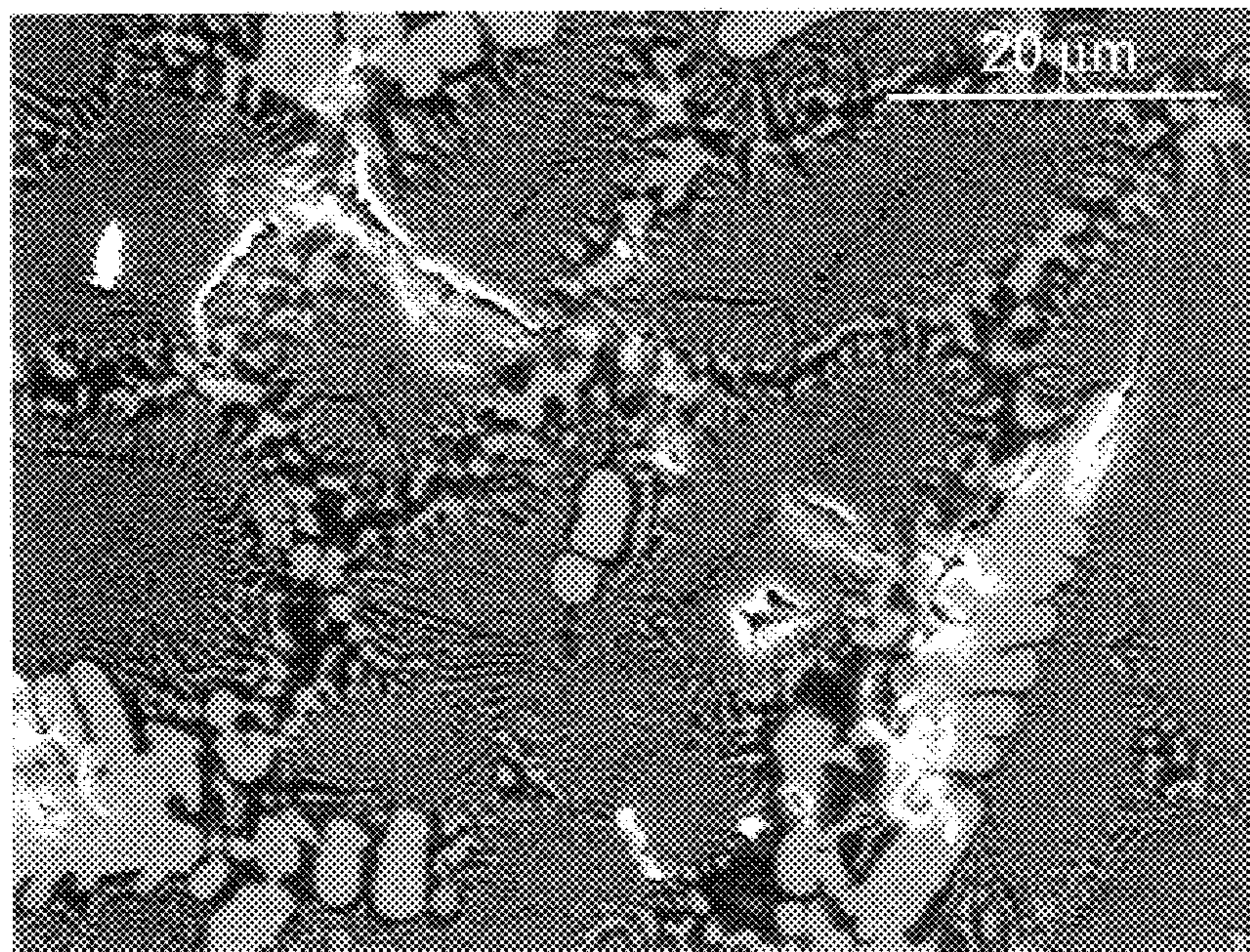


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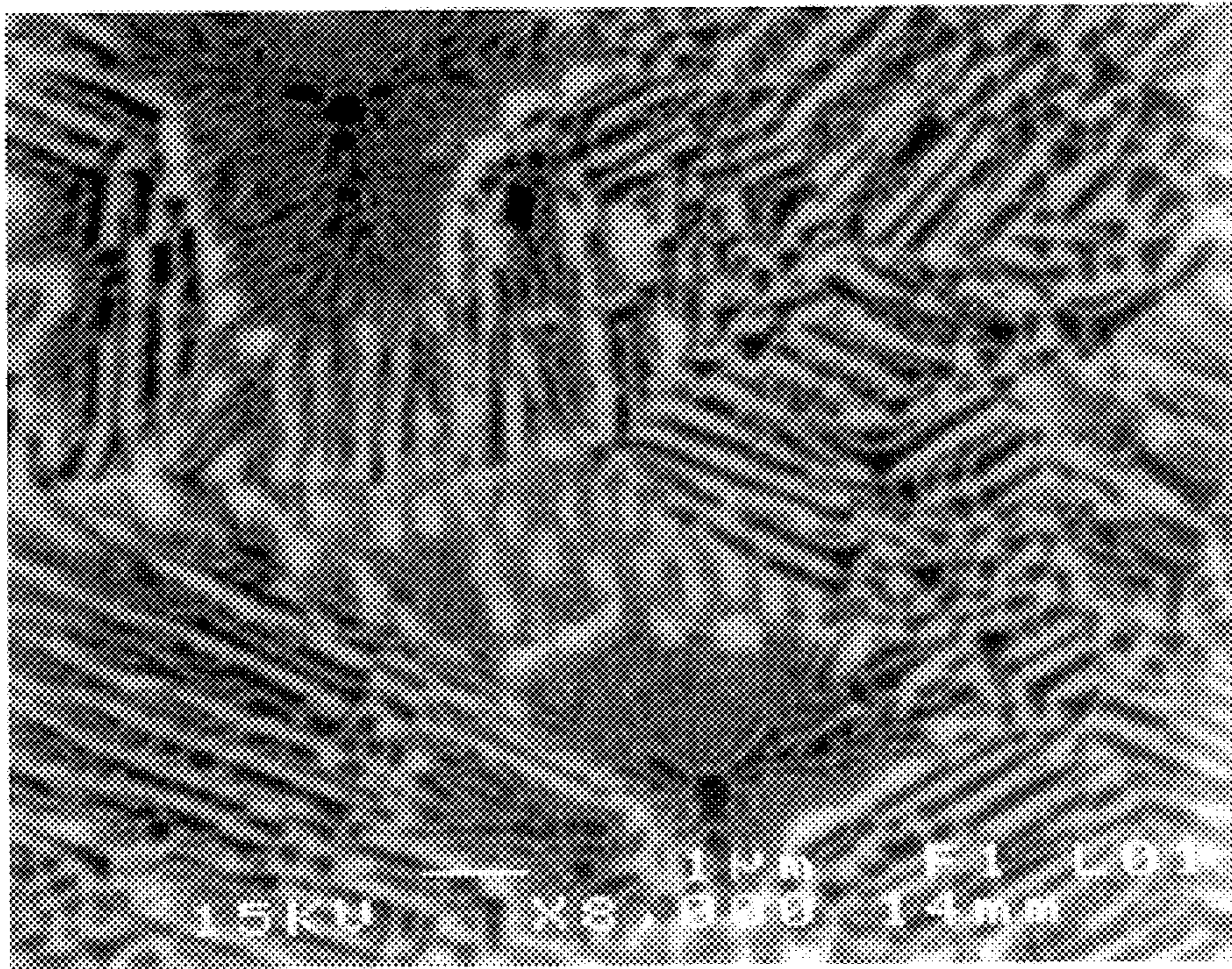


Fig. 19

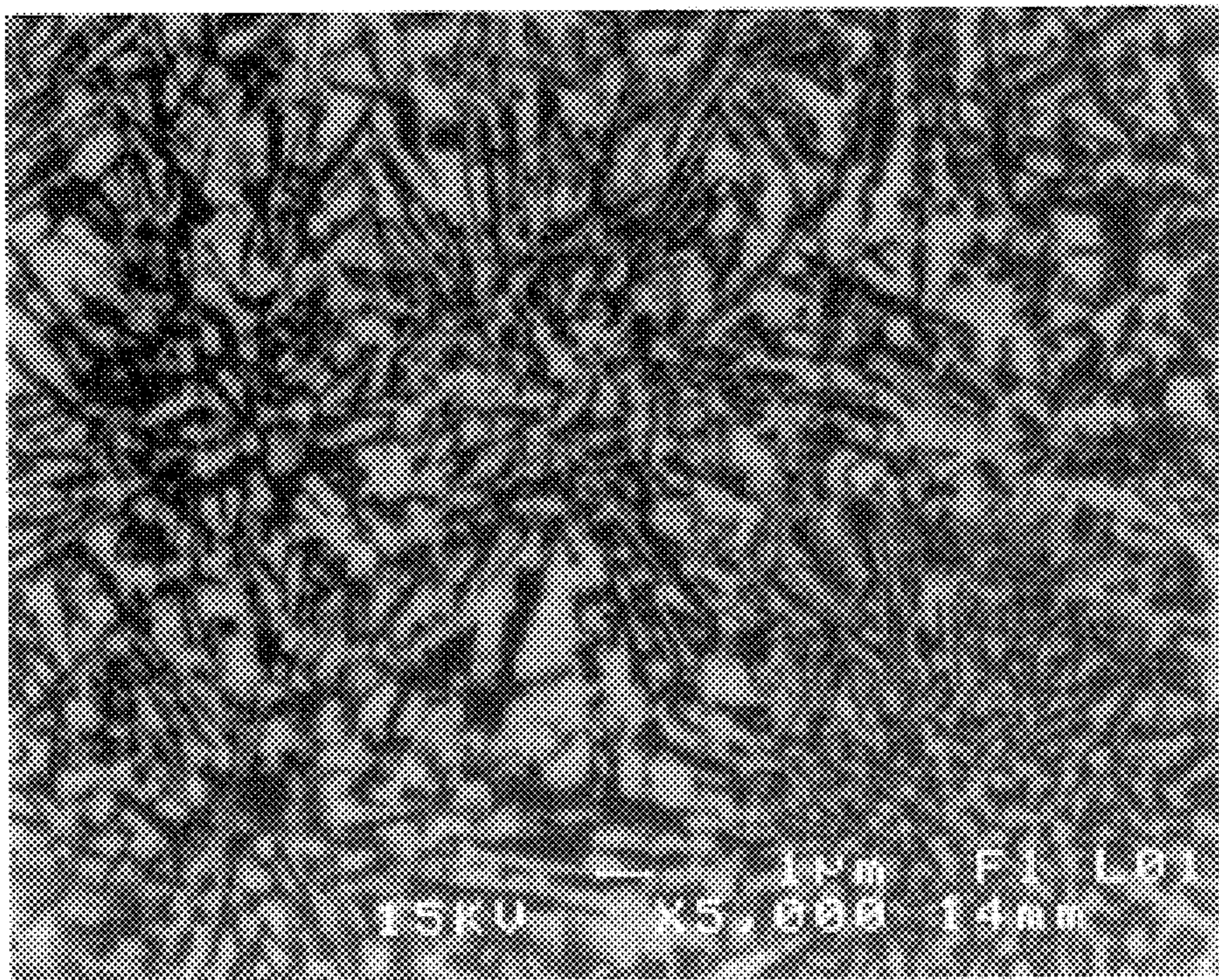


Fig. 20

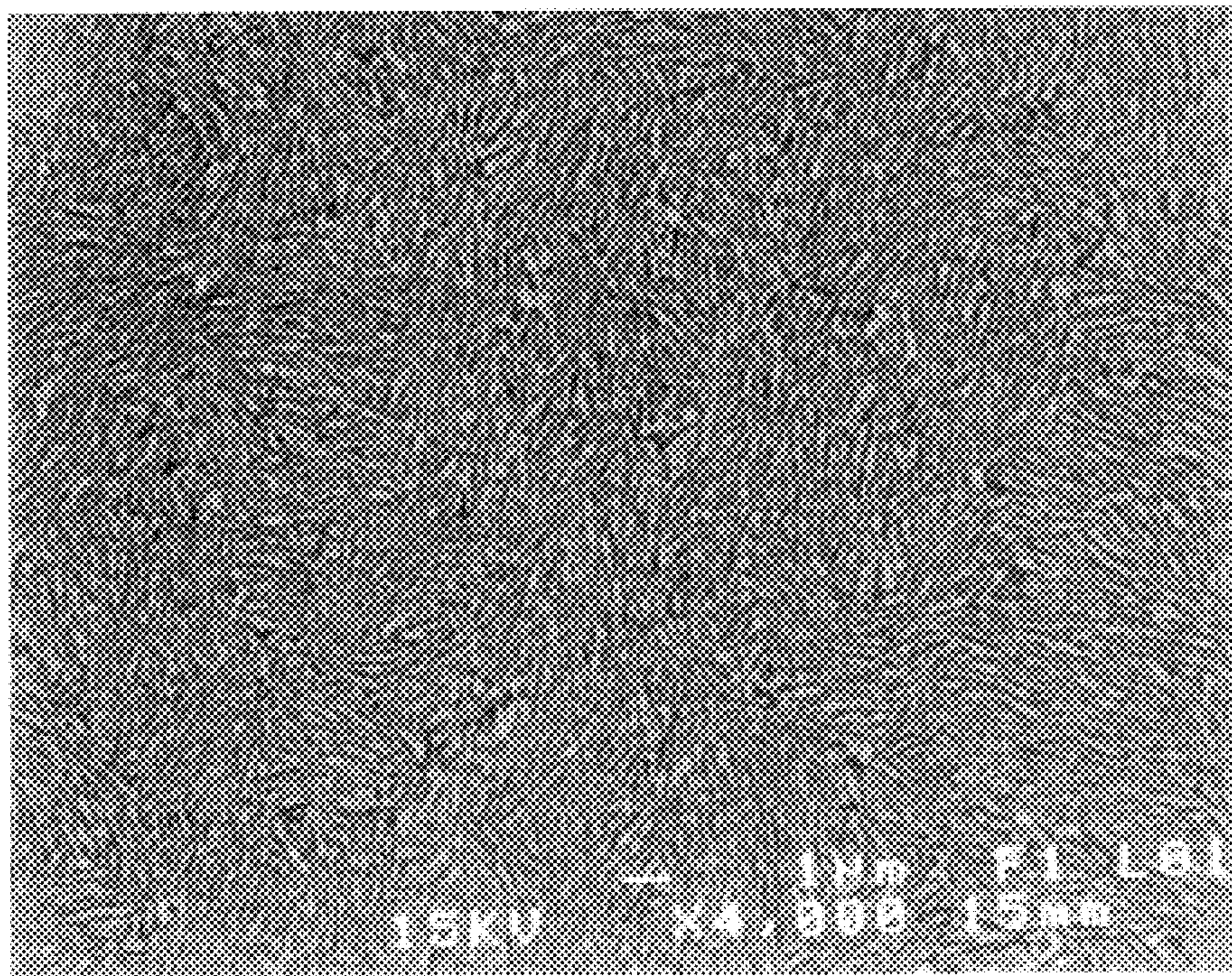


Fig. 21

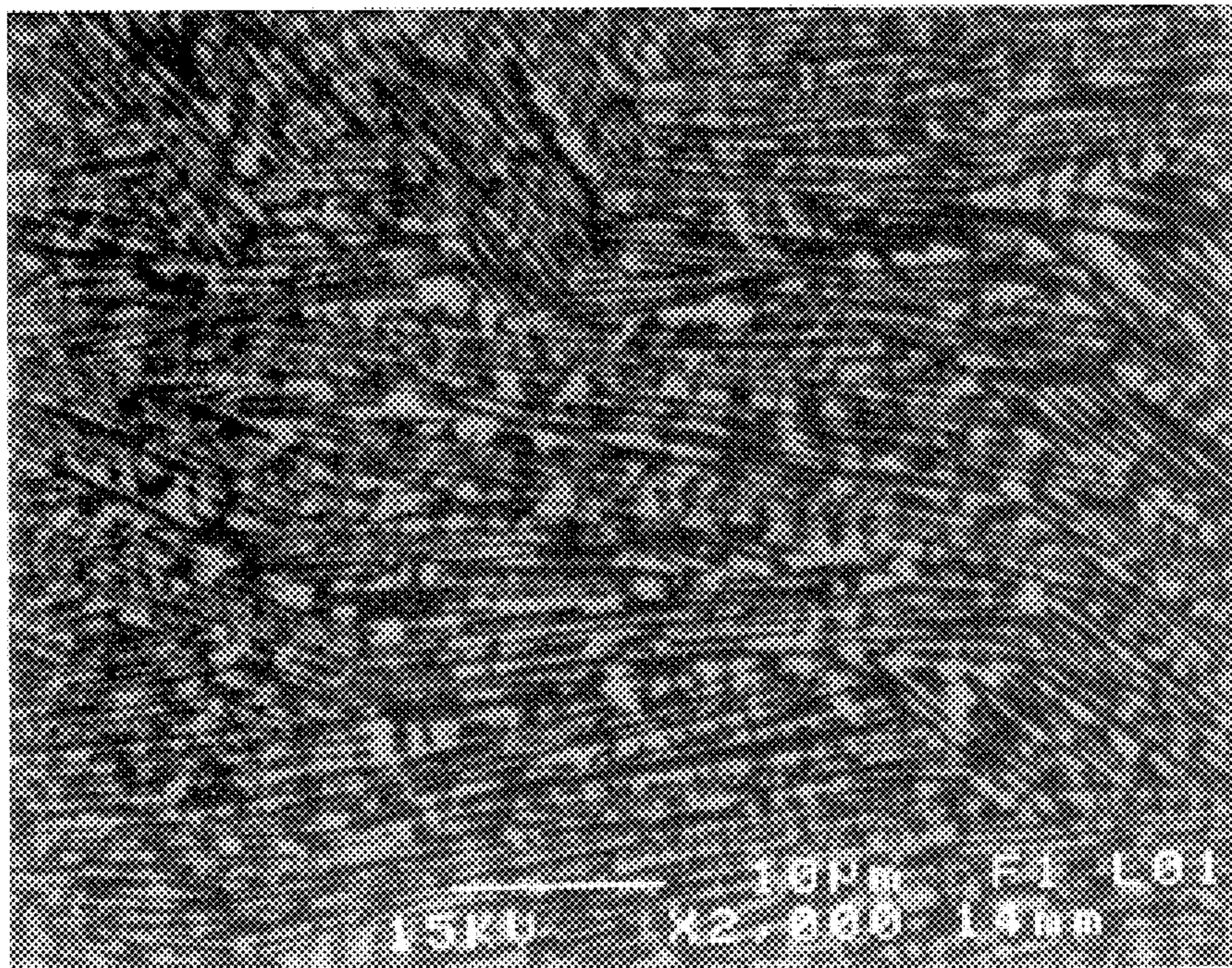


Fig. 22

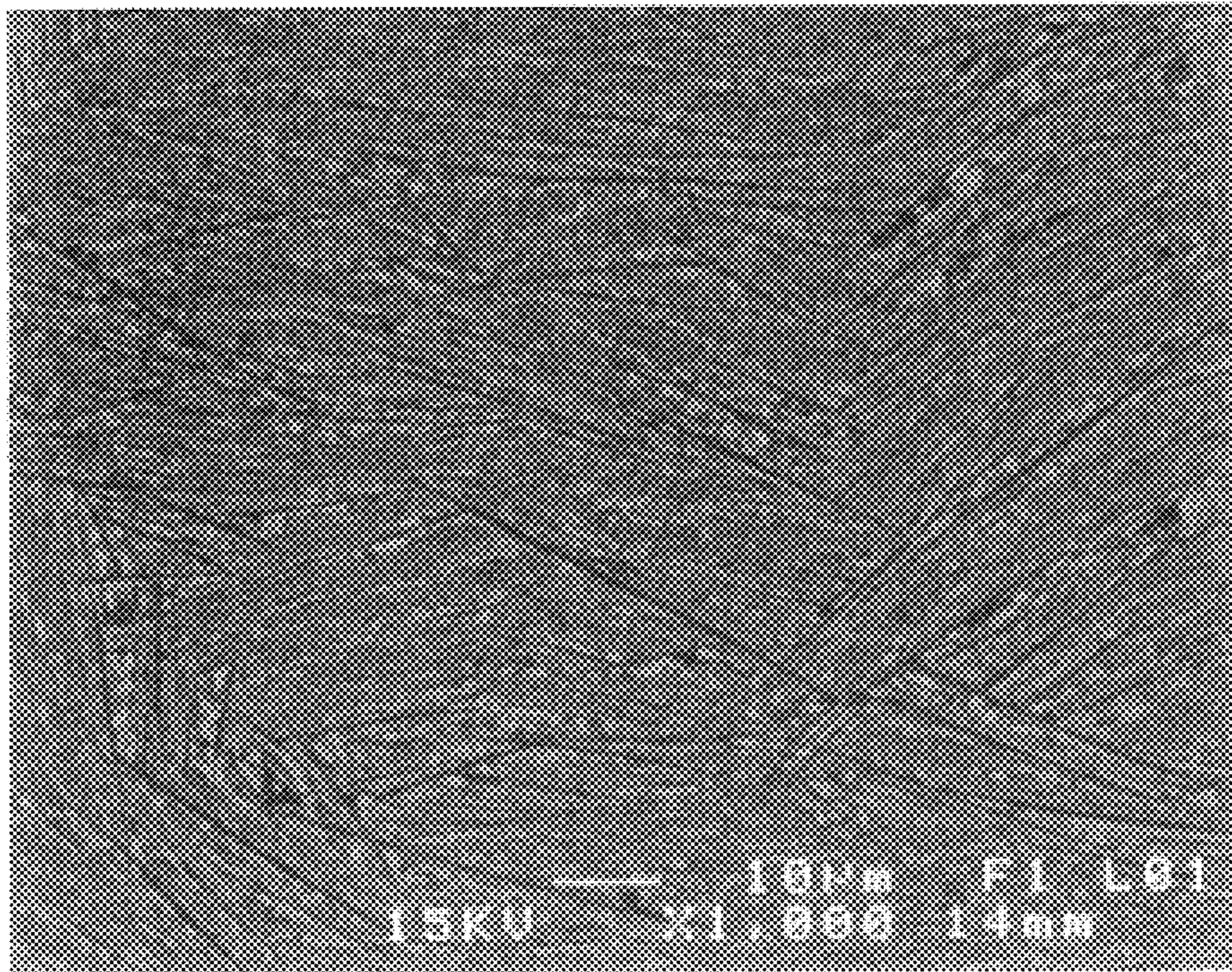


Fig. 23

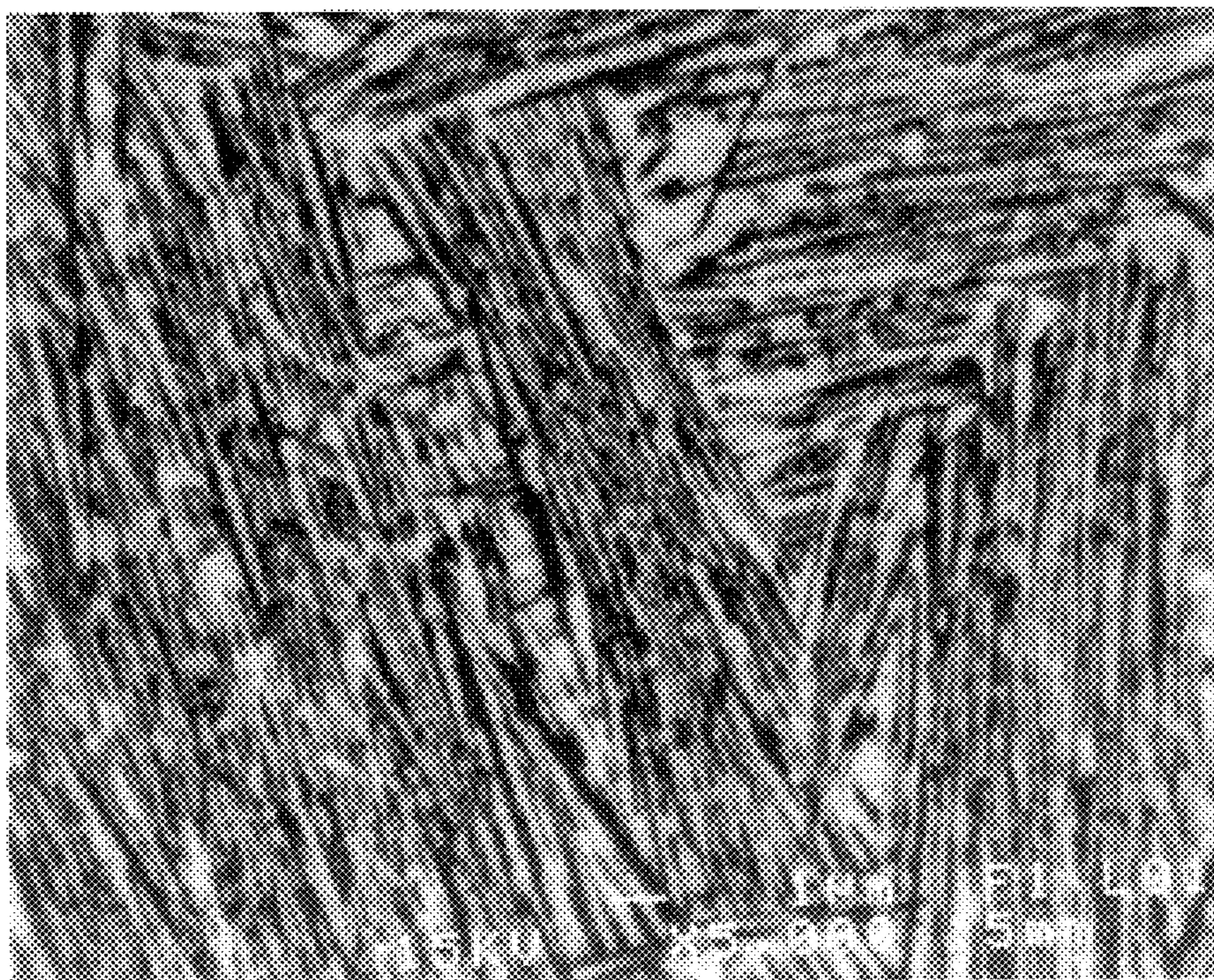


Fig. 24

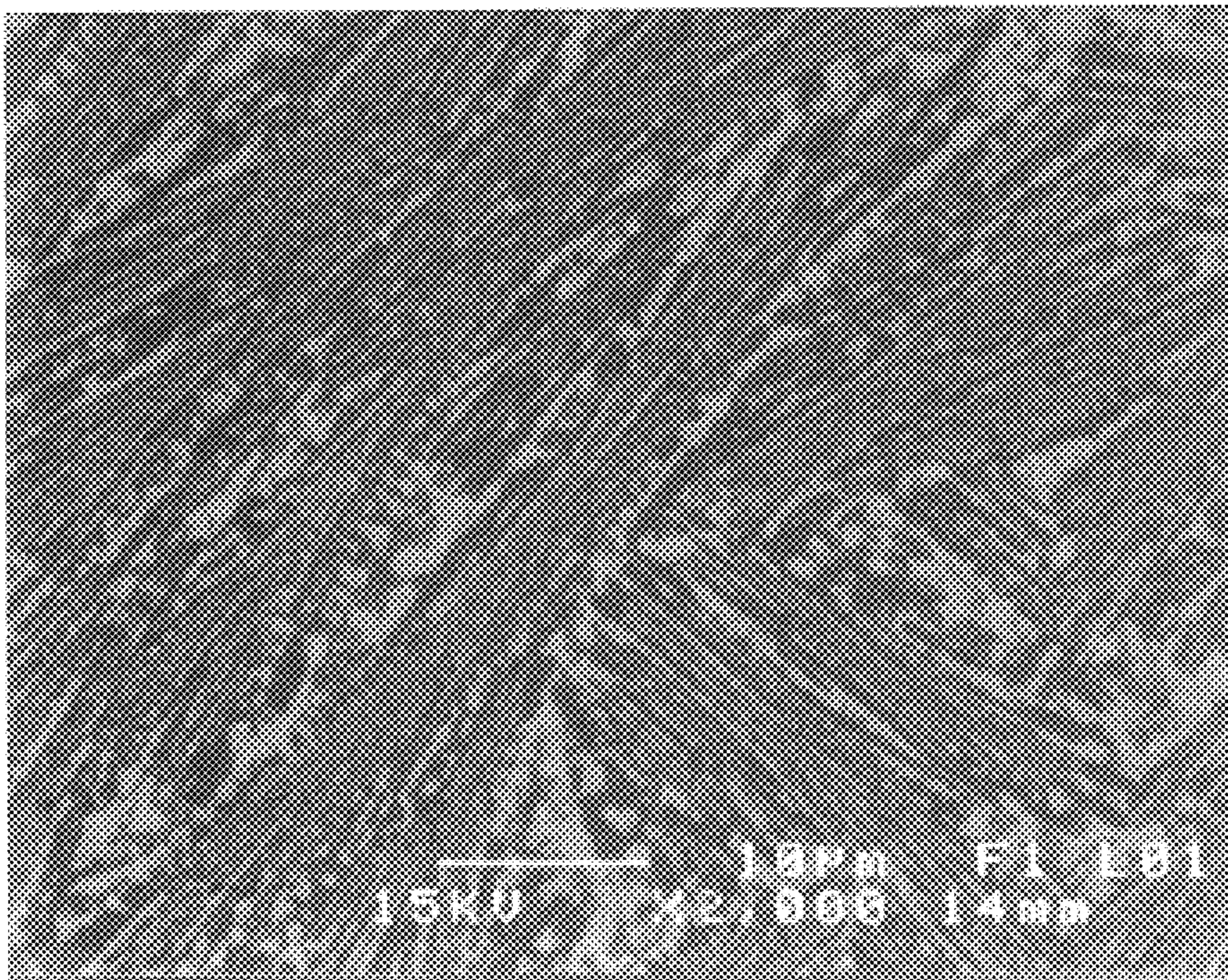


Fig. 25

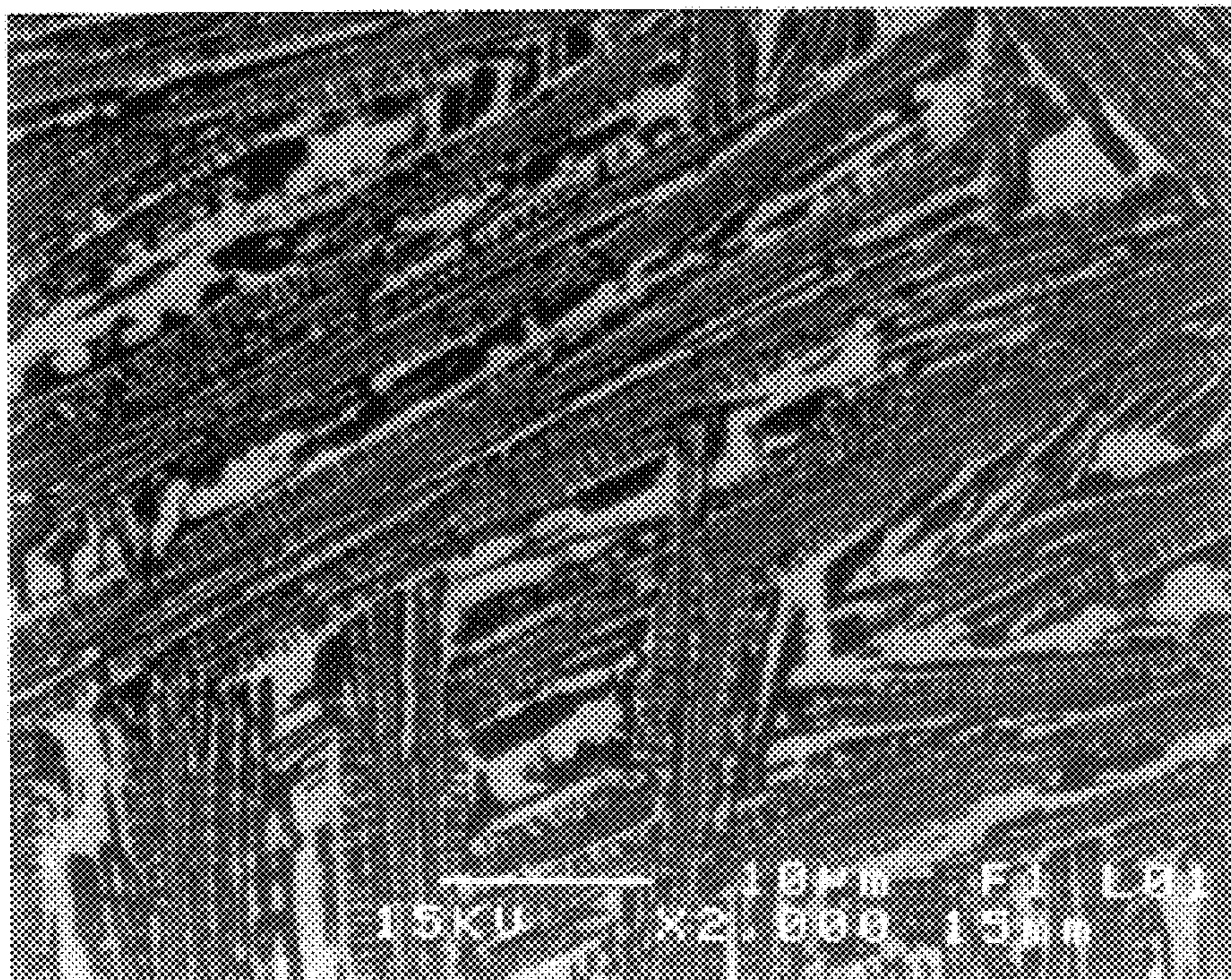


Fig. 26

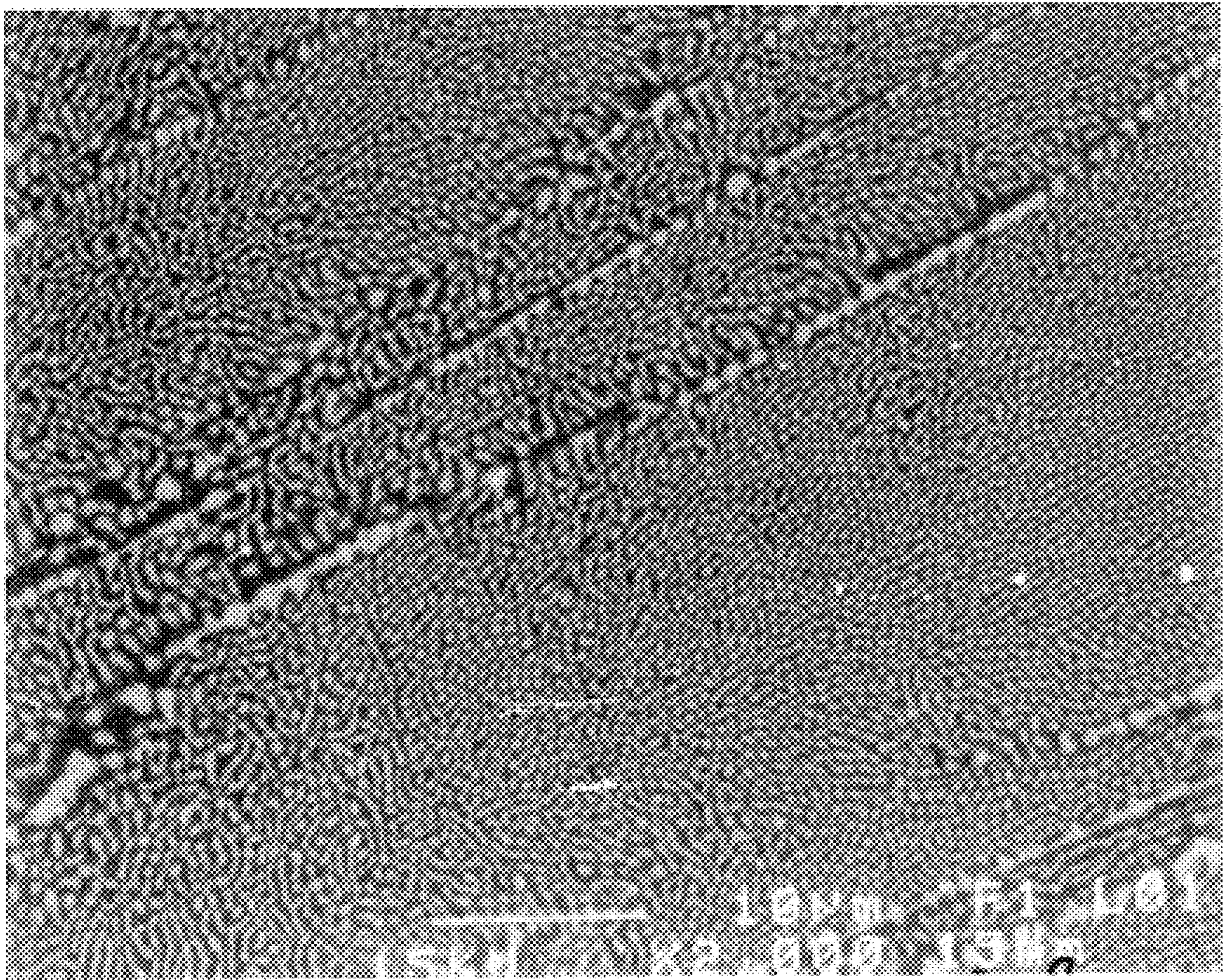


Fig. 27

FUSED Al_2O_3 -RARE EARTH OXIDE-ZR O_2 EUTECTIC MATERIALS

FIELD OF THE INVENTION

This invention pertains to fused material comprised of Al_2O_3 -rare earth oxide-Zr O_2 eutectics. Examples of useful articles comprising fused Al_2O_3 -rare earth oxide eutectic material include fibers and abrasive particles.

DESCRIPTION OF RELATED ART

A variety of fused eutectic metal oxide materials are known in the art, including binary and ternary eutectic materials. Fused eutectic metal oxide materials are typically made by charging a furnace with sources of the various metal oxides, as well as other desired additives, heating the material above its melting point, and cooling the melt to provide a solidified mass (see, e.g., U.S. Pat. No. 1,161,620 (Coulter), U.S. Pat. No. 1,192,709 (Tone), U.S. Pat. No. 1,247,337 (Saunders et al.), U.S. Pat. No. 1,268,533 (Allen), U.S. Pat. No. 2,424,645 (Baumann et al.) U.S. Pat. No. 3,891,408 (Rowse et al.), U.S. Pat. No. 3,781,172 (Pett et al.), U.S. Pat. No. 3,893,826 (Quinan et al.), U.S. Pat. No. 4,126,429 (Watson), U.S. Pat. No. 4,457,767 (Poon et al.), U.S. Pat. No. 5,143,522 (Gibson et al.), U.S. Pat. No. 5,023,212 (Dubots et. al), and U.S. Pat. No. 5,336,280 (Dubots et. al).

There is, however, a continuing desire for new materials which may offer performance characteristics (including combinations of characteristics) that are different than conventional materials, are easier to make, and/or cheaper to make.

SUMMARY OF THE INVENTION

The present invention provides a fused, crystalline eutectic material comprising eutectic of at least (a) crystalline Zr O_2 and (b) at least two of (i) crystalline Al_2O_3 , (ii) first crystalline complex Al_2O_3 -rare earth oxide, or (iii) second, different (i.e., different from the first crystalline complex Al_2O_3 -rare earth oxide), crystalline complex Al_2O_3 -rare earth oxide material.

One preferred eutectic material according to the present invention comprises eutectic of at least (a) crystalline Zr O_2 (b) crystalline Al_2O_3 , and crystalline complex Al_2O_3 -rare earth oxide. Another preferred eutectic material according to the present invention comprises eutectic of at least (a) crystalline Zr O_2 , (b) first crystalline complex Al_2O_3 -rare earth oxide, and (c) second, different, crystalline complex Al_2O_3 -rare earth oxide.

In another aspect, the present invention provides a fused, crystalline eutectic material comprising eutectic of at least (a) crystalline complex Al_2O_3 -rare earth oxide and (b) crystalline Zr O_2 .

In another aspect, a fused, crystalline material according to the present invention preferably comprises, on a theoretical oxide basis, at least 30 percent (or even at least 40, 50, 60, 70, or 80 percent) by weight Al_2O_3 , based on the total metal oxide content the material.

In this application:

“simple metal oxide” refers to a metal oxide comprised of a one or more of the same metal element and oxygen (e.g., Al_2O_3 , CeO_2 , MgO , SiO_2 , and Y_2O_3);

“complex metal oxide” refers to a metal oxide comprised of two or more different metal elements and oxygen (e.g., $\text{CeAl}_{11}\text{O}_{18}$, $\text{Dy}_3\text{Al}_5\text{O}_{12}$, MgAl_2O_4 , and $\text{Y}_3\text{Al}_5\text{O}_{12}$);

“complex Al_2O_3 -metal oxide” refers to a complex metal oxide comprised of, on a theoretical oxide basis, Al_2O_3 and one or more metal elements other than Al (e.g., $\text{CeAl}_{11}\text{O}_{18}$, $\text{Dy}_3\text{Al}_5\text{O}_{12}$, MgAl_2O_4 , and $\text{Y}_3\text{Al}_5\text{O}_{12}$);

“complex Al_2O_3 - Y_2O_3 ” refers to a complex metal oxide comprised of, on a theoretical oxide basis, Al_2O_3 and Y_2O_3 (e.g., $\text{Y}_3\text{Al}_5\text{O}_{12}$);

“complex Al_2O_3 -rare earth oxide” or “complex Al_2O_3 -REO” refers to a complex metal oxide comprised of, on a theoretical oxide basis, Al_2O_3 and rare earth oxide (e.g., $\text{CeAl}_{11}\text{O}_{18}$ and $\text{Dy}_3\text{Al}_5\text{O}_{12}$);

“rare earth oxides” refer to, on a theoretical oxide basis, CeO_2 , Dy_2O_3 , Er_2O_3 , Eu_2O_3 , Gd_2O_3 , Ho_2O_3 , La_2O_3 , Lu_2O_3 , Nd_2O_3 , Pr_6O_{11} , Sm_2O_3 , Th_4O_7 , Tm_2O_3 , and Yb_2O_3 ; and

“REO” means rare earth oxide.

In another aspect, the present invention provides a method for making fused, crystalline material according to the present invention, the method comprising:

melting at least one Al_2O_3 source, at least one rare earth oxide source, and at least one Zr O_2 source to provide a melt; and

converting the melt to the fused, crystalline material.

Fused crystalline material according to the present invention can be made, formed as, or converted into fibers or abrasive particles.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a Differential thermal analysis (DTA) plot and Thermogravimetric Analysis (TGA) plot of Comparative Example B fused material;

FIG. 2 is a DTA plot and TGA plot of Comparative Example C fused material;

FIG. 3 is a DTA plot and TGA plot of Comparative Example K fused material;

FIG. 4 is a DTA plot and TGA plot of Comparative Example F abrasive particles;

FIGS. 5–11 are scanning electron photomicrographs of polished cross-sections of Comparative Examples A–D and H–J fused material, respectively;

FIG. 12 is a scanning electron photomicrograph of a polished cross-section of Comparative Example K fused material;

FIG. 13 a scanning electron photomicrograph of a polished cross-section of a Comparative Example F abrasive particle;

FIGS. 14 and 15 are scanning electron photomicrographs of polished cross-sections of Comparative Example F abrasive particles after exposure to various heating conditions;

FIG. 16 is a scanning electron photomicrograph of a polished cross-sections of Comparative Example F abrasive particles after exposure to vitrified bonding material;

FIG. 17 and 18 are scanning electron photomicrographs of polished cross-sections of Comparative Example K material after exposure to various heating conditions;

FIGS. 19–26 are scanning electron photomicrographs of polished cross-sections of Example 1–8 fused material, respectively; and

FIG. 27 is a scanning electron photomicrograph of a polished cross-section of Comparative Example L fused material.

DETAILED DESCRIPTION

Fused crystalline material according to the present invention can be made, formed as, or converted into fibers,

reinforcing particles, abrasive particles; or coatings (e.g., protective coatings). The abrasive particles can be used be incorporated into an abrasive article, or in loose form. The fibers are useful, for example, as thermal insulation and reinforcing members in composites (e.g., ceramic, metal, or polymeric matrix composites).

In general, fused material according to the present invention can be made by heating the appropriate metal oxides sources to form a melt, preferably a homogenous melt, and then rapidly cooling the melt to provide a solidified mass.

More specifically, fused material according to the present invention can be made by charging a furnace with sources of (on a theoretical oxide basis) Al_2O_3 , rare earth oxide(s), ZrO_2 , and other optional additives (e.g., other metal oxides and processing aids). The metal oxide sources can be added to the furnace, for example, together and melted, or sequentially and melted.

For solidified melt material containing complex metal oxide(s), at least a portion of the metal oxide present in the melted metal oxide sources (i.e., the melt) react to form complex metal oxide(s) during formation process of the solidified material. For example, an Al_2O_3 source and a Yb_2O_3 source may react to form $\text{Yb}_3\text{Al}_5\text{O}_{12}$ (i.e., $5\text{Al}_2\text{O}_3 + 3\text{Yb}_2\text{O}_3 \rightarrow 2\text{Yb}_3\text{Al}_5\text{O}_{12}$). Similarly, for example, an source and an Er_2O_3 source may react to form $\text{Er}_3\text{Al}_5\text{O}_{12}$. Further, for example, an Al_2O_3 source and a Gd_2O_3 source may react to form GdAlO_3 (i.e., $\text{Al}_2\text{O}_3 + \text{Gd}_2\text{O}_3 \rightarrow 2\text{GdAlO}_3$). Similarly, for example, an Al_2O_3 source and a CeO_2 , Dy_2O_3 , Eu_2O_3 , La_2O_3 , Nd_2O_3 , Pr_2O_3 , or Sm_2O_3 source may react to form CeAlO_3 , $\text{Dy}_3\text{Al}_5\text{O}_{12}$, EuAlO_3 , LaAlO_3 , NdAlO_3 , PrAlO_3 , and SmAlO_3 , respectively. Further, for example, an Al_2O_3 source and a La_2O_3 source may react to form LaAlO_3 (i.e., $\text{Al}_2\text{O}_3 + \text{La}_2\text{O}_3 \rightarrow 2\text{LaAlO}_3$) and $\text{LaAl}_{11}\text{O}_{18}$ (i.e., $11\text{Al}_2\text{O}_3 + \text{La}_2\text{O}_3 \rightarrow 2\text{LaAl}_{11}\text{O}_{18}$). Similarly, for example, an Al_2O_3 source and CeO_2 , Eu_2O_3 , Nd_2O_3 , Pr_2O_3 , or Sm_2O_3 source may react to form $\text{CeAl}_{11}\text{O}_{18}$, $\text{EuAl}_{11}\text{O}_{18}$, $\text{NdAl}_{11}\text{O}_{18}$, $\text{PrAl}_{11}\text{O}_{18}$, and $\text{SmAl}_{11}\text{O}_{18}$, respectively.

Depending upon the relative proportions of Al_2O_3 , rare earth oxide, and/or and ZrO_2 the resultant solidified material, may comprise:

- (a) crystalline Al_2O_3 -complex Al_2O_3 .metal oxide (complex Al_2O_3 .metal oxide is, for example, $\text{Dy}_3\text{Al}_5\text{O}_{12}$, $\text{Er}_3\text{Al}_5\text{O}_{12}$, GdAlO_3 , or $\text{Yb}_3\text{Al}_5\text{O}_{12}$)— ZrO_2 eutectic and crystalline Al_2O_3 ;
- (b) crystalline Al_2O_3 -complex Al_2O_3 .metal oxide (again complex Al_2O_3 .metal oxide is, for example, $\text{Dy}_3\text{Al}_5\text{O}_{12}$, $\text{Er}_3\text{Al}_5\text{O}_{12}$, GdAlO_3 , or $\text{Yb}_3\text{Al}_5\text{O}_{12}$)— ZrO_2 eutectic;
- (c) crystalline Al_2O_3 -complex Al_2O_3 .metal oxide (again complex Al_2O_3 .metal oxide is, for example, $\text{Dy}_3\text{Al}_5\text{O}_{12}$, $\text{Er}_3\text{Al}_5\text{O}_{12}$, GdAlO_3 , or $\text{Yb}_3\text{Al}_5\text{O}_{12}$)— ZrO_2 eutectic and crystalline complex Al_2O_3 .metal oxide (again, complex Al_2O_3 .metal oxide is, for example, $\text{Dy}_3\text{Al}_5\text{O}_{12}$, $\text{Er}_3\text{Al}_5\text{O}_{12}$, GdAlO_3 , or $\text{Yb}_3\text{Al}_5\text{O}_{12}$); and/or
- (d) crystalline complex Al_2O_3 .metal oxide (again, complex Al_2O_3 .metal oxide is, for example, $\text{Dy}_3\text{Al}_5\text{O}_{12}$, $\text{Er}_3\text{Al}_5\text{O}_{12}$, GdAlO_3 , or $\text{Yb}_3\text{Al}_5\text{O}_{12}$)— ZrO_2 eutectic and crystalline ZrO_2 .

If Al_2O_3 reacts with rare earth oxide to form two complex metal oxides, the resulting solidified material, depending upon the relative proportions of Al_2O_3 and rare earth oxide, may comprise:

- (a) first crystalline complex Al_2O_3 .metal oxide (e.g., CeAlO_3 , EuAlO_3 , LaAlO_3 , NdAlO_3 , PrAlO_3 , or SmAlO_3)-second, different (i.e., different than the first

crystalline complex Al_2O_3 .metal oxide), crystalline complex Al_2O_3 .metal oxide (e.g., $\text{CeAl}_{11}\text{O}_{18}$, $\text{EuAl}_{11}\text{O}_{18}$, $\text{LaAl}_{11}\text{O}_{18}$, $\text{NdAl}_{11}\text{O}_{18}$, $\text{PrAl}_{11}\text{O}_{18}$, or $\text{SmAl}_{11}\text{O}_{18}$, respectively ZrO_2 eutectic and first crystalline complex Al_2O_3 .metal oxide (again, e.g., CeAlO_3 , EuAlO_3 , LaAlO_3 , NdAlO_3 , PrAlO_3 , or SmAlO_3);

- (b) first crystalline complex Al_2O_3 .metal oxide (again, e.g., CeAlO_3 , EuAlO_3 , LaAlO_3 , NdAlO_3 , PrAlO_3 , or SmAlO_3)-second, different, crystalline complex Al_2O_3 .metal oxide (again, e.g., $\text{CeAl}_{11}\text{O}_{18}$, $\text{EuAl}_{11}\text{O}_{18}$, $\text{LaAl}_{11}\text{O}_{18}$, $\text{NdAl}_{11}\text{O}_{18}$, $\text{PrAl}_{11}\text{O}_{18}$, or $\text{SmAl}_{11}\text{O}_{18}$, respectively)— ZrO_2 eutectic;

- (c) first crystalline complex Al_2O_3 .metal oxide (again, e.g., CeAlO_3 , EuAlO_3 , LaAlO_3 , NdAlO_3 , PrAlO_3 , or SmAlO_3)-second, different, crystalline complex Al_2O_3 .metal oxide (again, e.g., $\text{CeAl}_{11}\text{O}_{18}$, $\text{EuAl}_{11}\text{O}_{18}$, $\text{LaAl}_{11}\text{O}_{18}$, $\text{NdAl}_{11}\text{O}_{18}$, $\text{PrAl}_{11}\text{O}_{18}$, or $\text{SmAl}_{11}\text{O}_{18}$, respectively)— ZrO_2 eutectic and second, different, crystalline complex Al_2O_3 .metal oxide (again, e.g., $\text{CeAl}_{11}\text{O}_{18}$, $\text{EuAl}_{11}\text{O}_{18}$, $\text{LaAl}_{11}\text{O}_{18}$, $\text{NdAl}_{11}\text{O}_{18}$, $\text{PrAl}_{11}\text{O}_{18}$, or $\text{SmAl}_{11}\text{O}_{18}$); and/or

- (d) first crystalline complex Al_2O_3 .metal oxide (again, e.g., CeAlO_3 , EuAlO_3 , LaAlO_3 , NdAlO_3 , PrAlO_3 , or SmAlO_3)-second, different, crystalline complex Al_2O_3 .metal oxide (again, e.g., $\text{CeAl}_{11}\text{O}_{18}$, $\text{EuAl}_{11}\text{O}_{18}$, $\text{LaAl}_{11}\text{O}_{18}$, $\text{NdAl}_{11}\text{O}_{18}$, $\text{PrAl}_{11}\text{O}_{18}$, or $\text{SmAl}_{11}\text{O}_{18}$, respectively)— ZrO_2 eutectic and crystalline ZrO_2 .

It is understood, however, the particular phases formed are dependent upon several factors including the melt composition and solidification conditions. Typically it is preferred that the composition of the melt and the solidification conditions are such that a large portion of the resulting solidified material is occupied by eutectic (i.e., the formulation of the solidified material corresponds to close to eutectic proportions of the various metal oxide phases that present in the material). Although not wanting to be bound by theory, some metastable conditions during formation of the solidified material may lead to the formation of alternative eutectic. For example, if under normal, stable conditions the eutectic that forms is $\text{Al}_2\text{O}_3/\text{Dy}_3\text{Al}_5\text{O}_{12}/\text{ZrO}_2$, under some metastable conditions $\text{Al}_2\text{O}_3/\text{DyAlO}_3/\text{ZrO}_2$ eutectic may form in place of, or in addition to $\text{Al}_2\text{O}_3/\text{Dy}_3\text{Al}_5\text{O}_{12}/\text{ZrO}_2$ eutectic.

It is also within the scope of the present invention to substitute a portion of the rare earth and/or aluminum cations in the complex Al_2O_3 .REO (e.g., $\text{Dy}_3\text{Al}_5\text{O}_{12}$, $\text{Er}_3\text{Al}_5\text{O}_{12}$, GdAlO_3 , $\text{Yb}_3\text{Al}_5\text{O}_{12}$, or $\text{LaAl}_{11}\text{O}_{18}$) with other cations. For example, a portion of the Al cations in a complex Al_2O_3 .REO may be substituted with at least one cation of an element selected from the group consisting of: Cr, Ti, Sc, Fe, Mg, Ca, Si, Co, and combinations thereof. For example, a portion of the rare earth cations in a complex Al_2O_3 .REO may be substituted with at least one cation of an element selected from the group consisting of: Y, Fe, Ti, Mn, V, Cr, Co, Ni, Cu, Mg, Ca, Sr, and combinations thereof. Similarly, it is also within the scope of the present invention to substitute a portion of the aluminum cations in alumina. For example, Cr, Ti, Sc, Fe, Mg, Ca, Si, and Co can substitute for aluminum in alumina structure. The substitution of cations as described above may affect the properties (e.g. hardness, toughness, strength, thermal conductivity, etc.) of the fused material.

Further, other eutectics will be apparent to those skilled in the art after reviewing the present disclosure. For example, phase diagrams depicting various eutectics are known in the art.

Fused material according to the present invention typically is comprised of eutectic colonies. An individual colony contains generally homogeneous microstructural characteristics (e.g., similar size and orientation of crystals of constituent phases within a colony). Typically, impurities, if present, in the fused, crystalline material according to the present invention, tend to segregate to colony boundaries, and may be present alone and/or as reaction products (e.g., as a complex Al_2O_3 -metal oxide and/or a complex REO-metal oxide) as crystalline and/or amorphous (glass) phase(s).

In general, the phases making up the eutectic colonies include (a) single crystals of three different metal oxides (e.g., single crystals of each of Al_2O_3 , $\text{Yb}_3\text{Al}_5\text{O}_{12}$, and ZrO_2), (b) single crystals of two of the metal oxides (e.g., single crystal Al_2O_3 and single crystal ZrO_2) and a plurality of crystals of a different metal oxide (e.g., polycrystalline $\text{Y}_3\text{Al}_5\text{O}_{12}$), (c) a single crystal of one of the metal oxide (e.g., single crystal Al_2O_3 or ZrO_2) and a plurality of crystals of two different metal oxide (e.g., polycrystalline $\text{Yb}_3\text{Al}_5\text{O}_{12}$ and polycrystalline ZrO_2), or (d) three different polycrystalline metal oxides (e.g., polycrystalline Al_2O_3 , polycrystalline $\text{Yb}_3\text{Al}_5\text{O}_{12}$, and polycrystalline ZrO_2).

The colonies may be in any of a variety of shapes, typically, ranging from essentially spherical to columnar. The composition, phase, and/or microstructure (e.g., crystallinity (i.e., single crystal or polycrystalline) and crystal size) of each colony may be the same or different. The orientation of the crystals inside the colonies may vary from one colony to another. The phases making up some eutectic colonies may be present in a variety of shapes such as, for example, rod or platelet-like to "chinese script"-like. Such differences between colonies may even be present between adjacent colonies.

The microstructure may also be a mixture of two constituent phases in a "chinese script" arrangement, with a third phase being present, for example, as rods or plates. Alternatively, for example, two constituent phases may be present as an interpenetrating network with a third phase present, for example, as plates or rods.

The number of colonies, their sizes and compositions are affected, for example, by the melt composition and solidification conditions. Although not wanting to be bound by theory, it is believed that the closer the melt composition is to the exact eutectic composition, the smaller the number of colonies that are formed. In another aspect, however, it is believed that slow, unidirectional solidification of the melt also tends to minimize the number of colonies formed, while multidirectional solidification with relatively higher cooling rates tends to increase the number of colonies formed. The solidification rate (i.e., cooling rate) of the melt and/or multidirectional solidification of the melt tend to affect the type and/or number of microstructural imperfections (e.g., pores) present in the resulting fused material. For example, although not wanting to be bound by theory, relatively rapid solidification (i.e., solidification with relatively high cooling rates) and/or multidirectional solidification tend to lead to an increase in the type and/or number of microstructural imperfections (e.g., pores) present in the resulting fused material. Relatively slow solidification, however, tends to lead to an increase in the size of the colonies, and/or crystals present in the solidified material; although it may be possible through slow and controlled cooling, for example, to eliminate formation of colonies. Hence, in selecting the cooling rate and/or degree of multidirectional solidification, there may be a need to increase or decrease the cooling rate to obtain the optimal balance of desirable and undesirable microstructural characteristics associated with the various cooling rates.

Further, for a given composition, the size of the colonies and phases present within the colonies tends to decrease as the cooling rate of the melt increases. Typically, the eutectic colonies in fused material according to the present invention are, on average, less than 100 micrometers, preferably, less than 50 micrometers, wherein such size for a given colony is the average of the two largest dimensions measured from a polished cross-section of the colony, as viewed with a scanning electron microscope (SEM). Typically, the smallest dimension of the crystalline phases making up the eutectic in a colony, as measured from a polished cross-section of the colony viewed with an SEM, is up to 10 micrometers; preferably, up to 5 micrometers; more preferably, up to 1 micrometer, or even up to 0.5 micrometer.

Some fused materials according to the present invention also include primary crystals of at least one of the metal oxide phases making up the eutectic constituent of the material. For example, if the eutectic portion is made up of an Al_2O_3 phase, a complex Al_2O_3 -REO (e.g., $\text{Yb}_3\text{Al}_5\text{O}_{12}$ phase, and ZrO_2 phase, the microstructure may also include primary crystals of Al_2O_3 , $\text{Yb}_3\text{Al}_5\text{O}_{12}$, or ZrO_2 , which is believed to occur when the composition of the melt from which the fused material is formed is rich in, on a theoretical oxide basis, Al_2O_3 , Yb_2O_3 , or ZrO_2 , respectively.

The formation of the primary crystals is believed to result from a deviation from the particular eutectic proportions. The greater the deviation, the larger the overall fraction of primary crystals. The primary crystals may be found in a variety of shapes, typically ranging from rod-like structures to dendritic-like structures. Although not wanting to be bound by theory, it is believed that the presence and/or formation of a primary crystal(s) adjacent to a colony may affect the resulting microstructure of the colony. In some cases it may be advantageous (e.g., for an abrasive particle increased abrading performance) to have primary crystals (e.g., primary Al_2O_3 crystals) present in the fused material. It is also believed, however, for abrasive particles, for example, that the abrading performance of an abrasive particle tends to decrease as the size of the primary crystals increase.

Further, although not wanting to be bound by theory, it is believed that small additions (e.g., less than 5 percent by weight) of metal oxides other than those making up the eutectic may affect colony boundaries, and in turn affect properties (e.g., hardness and toughness) of the fused material.

Sources of (on a theoretical oxide basis) Al_2O_3 for making fused material according to the present invention include those known in the art for making conventional fused alumina and alumina-zirconia materials. Commercially available Al_2O_3 sources include bauxite (including both natural occurring bauxite and synthetically produced bauxite), calcined bauxite, hydrated aluminas (e.g., boehmite, and gibbsite), Bayer process alumina, aluminum ore, gamma alumina, alpha alumina, aluminum salts, aluminum nitrates, and combinations thereof. The Al_2O_3 source may contain, or only provide, Al_2O_3 . Alternatively, the Al_2O_3 source may contain, or provide Al_2O_3 , as well as one or more metal oxides other than Al_2O_3 (including materials of or containing complex Al_2O_3 -metal oxides (e.g., $\text{Dy}_3\text{Al}_5\text{O}_{12}$, $\text{Y}_3\text{Al}_5\text{O}_{12}$, $\text{CeAl}_{11}\text{O}_{18}$, etc.)).

Commercially available sources of rare earth oxides for making fused material according to the present invention include rare earth oxide powders, rare earth metals, rare earth-containing ores (e.g., bastnasite and monazite), rare earth salts, rare earth nitrates, and rare earth carbonates. The rare earth oxide(s) source may contain, or only provide, rare

earth oxide(s). Alternatively, the rare earth oxide(s) source may contain, or provide rare earth oxide(s), as well as one or more metal oxides other than rare earth oxide(s) (including materials of or containing complex rare earth oxide.other metal oxides (e.g., $\text{Dy}_3\text{Al}_5\text{O}_{12}$, $\text{CeAl}_{11}\text{O}_{18}$, etc.)).

Commercially available sources of (on a theoretical oxide basis) ZrO_2 for making fused material according to the present invention include zirconium oxide powders, zircon sand, zirconium, zirconium-containing ores, and zirconium salts (e.g., zirconium carbonates, acetates, nitrates, chlorides, hydroxides, and combinations thereof). In addition, or alternatively, the ZrO_2 source may contain, or provide ZrO_2 , as well as other metal oxides such as hafnia.

Optionally, fused material according to the present invention further comprise other oxide metal oxides (i.e., metal oxides other than Al_2O_3 rare earth oxide(s), and ZrO_2). The addition of certain metal oxides may alter the crystalline structure or microstructure of the resulting fused material. For example, although not wishing to be bound by any theory, it is theorized that certain metal oxides or metal oxide containing compounds (even when used in relatively small amounts, for example, even 0.01 to 5 percent by weight, based on the total metal oxide content of the fused material) may be present at the boundaries between the eutectic colonies. The presence of these metal oxides, which may be in the form of reaction products together or with the Al_2O_3 , rare earth oxide(s), and/or ZrO_2 may affect the fracture characteristics and/or microstructure of the fused material, and/or properties of the fused material. The optional metal oxides may also act as a processing aid, for example, to increase the density of the fused material, by decreasing the size and/or number of pores in the fused material. The optional metal oxides may also act as a processing aid, for example, to increase or decrease the effective melting temperature of the melt. Thus certain metal oxides may be added for processing reasons.

It may be desirable to add metal oxides (e.g., Y_2O_3 , TiO_2 , CaO , and MgO) that are known to stabilize tetragonal/cubic form of ZrO_2 . In some embodiments of materials according to the present invention, crystalline ZrO_2 is stabilized by an oxide other than the rare earth oxide present in said crystalline complex Al_2O_3 .rare earth oxide. For example, for LaAlO_3 — $\text{LaAl}_{11}\text{O}_{18}$ — ZrO_2 eutectic, the ZrO_2 may be stabilized, for example, with Y_2O_3 .

Fused material according to the present invention typically comprise less than 50 percent by weight (more typically, less than 20 percent by weight; in some cases in the range from 0.01 to 5 percent by weight, in other cases from 0.1 to 1 percent by weight) of metals oxides (on a theoretical oxide basis) other than alumina rare earth oxides, and zirconia, based on the total metal oxide content of the fused material. Sources of the other metal oxides are also readily commercially available.

Examples of optional metal oxides include, on a theoretical oxide basis, BaO , CaO , Cr_2O_3 , CoO , Fe_2O_3 , HfO_2 , Li_2O , MgO , MnO , NiO , SiO_2 , TiO_2 , Na_2O , Sc_2O_3 , SrO , V_2O_3 , ZnO , Y_2O_3 , and combinations thereof. Further, with regard to Y_2O_3 , commercially available sources of (on a theoretical oxide basis) Y_2O_3 for making fused material according to the present invention include yttrium oxide powders, yttrium, yttrium-containing ores, and yttrium salts (e.g., yttrium carbonates, nitrates, chlorides, hydroxides, and combinations thereof). The Y_2O_3 source may contain, or only provide, Y_2O_3 . Alternatively, the Y_2O_3 source may contain, or provide Y_2O_3 , as well as one or more metal oxides other than Y_2O_3 (including materials of or containing complex Y_2O_3 .metal oxides (e.g., $\text{Y}_3\text{Al}_5\text{O}_{12}$)).

Metal oxide sources for making fused material according to the present invention also include fused abrasive particles (e.g., fused alumina abrasive particles) or other fused material (e.g., fused alumina material) having the same composition or different composition(s), which together with remaining metal oxide sources, provide the desired composition of the fused material.

A reducing agent, such as a carbon source may be added to reduce impurities during the melting process. Examples of carbon sources include: coal, graphite, petroleum coke, or the like. Typically, the amount of carbon included in the charge to the furnace is up 5% by weight of the charge; more typically, up to 3% by weight, and more typically, up to 2% by weight. Iron may also be added to the furnace charge to aid in the removal of impurities. The iron can combine with the impurities to make a material that can be removed magnetically, for example, from the melt or crushed solidified material.

It is also within the scope of the present invention to include metal borides, carbides, nitrides, and combinations thereof in the fused, crystalline material according to the present invention. Such materials may even be present within (e.g., as inclusions) the eutectic material. Examples of metal borides, carbides and nitrides may include titanium diboride, aluminum carbide, aluminum nitride, titanium carbide, titanium nitride, silicon carbide, boron carbide, and boron nitride. Such materials are known in the art, and are commercially available.

The particular selection of metal oxide sources and other additives for making fused material according to the present invention typically takes into account, for example, the desired composition and microstructure of the resulting fused material, the desired physical properties (e.g., hardness or toughness) of the resulting fused material, avoiding or minimizing the presence of undesirable impurities, the desired characteristics of the resulting fused material, and/or the particular process (including equipment and any purification of the raw materials before and/or during fusion and/or solidification) being used to prepare the fused material.

The metal oxide sources and other additives can be in any form suitable to the process and equipment being used to make the fused material. The raw materials can be fused using techniques and equipment known in the art for making conventional fused alumina and alumina-zirconia abrasive particles (see, e.g., U.S. Pat. No. 3,781,172 (Pett et al.), U.S. Pat. No. 3,891,408 (Rowse et al.), U.S. Pat. No. 4,035,162 (Brothers et al.), U.S. Pat. No. 4,070,796 (Scott), U.S. Pat. No. 4,073,096 (Ueltz et al.), U.S. Pat. No. 4,126,429 (Watson), U.S. Pat. No. 4,457,767 (Poon et al.), U.S. Pat. No. 5,143,522 (Gibson et al.), and Re. 31,128 (Walker et al.), the disclosures of which are incorporated herein by reference).

Examples of furnaces for melting the metal oxide sources and other additives include arc furnaces, pig furnaces, arc tapping furnaces, electric furnaces, electric arc furnaces, and gas fired furnaces. Suitable electric furnaces include those in which the electrodes are arranged to create a "kissing arc", wherein the lower tip of the electrodes are not in contact within the molten mass, as well as those in which the electrodes are submerged in the molten mass to provide resistance heating via current passing through the melt.

The furnace may have a lining (sometimes referred to as a "shell" or "skeleton") that covers the inside of the furnace walls. The lining may be made from a material dissimilar to the desired fused material composition. Typically, however it is preferred that the furnace lining is made from a

composition or material similar, sometimes nearly identical or identical to the composition of the fused material. Thus during processing, if the outer (exposed) surface of the lining melts, the potential contamination of the melt is reduced or minimized.

For some metal oxide sources and other additives, it may also be desirable to preheat feed prior to charging it into the furnace, or otherwise combining it with other metal oxide sources and other additives. For example, if carbonate, nitrate or other salts are used as the metal oxide source, it may be desirable to calcine (e.g., by heating them in air at about 400–1000° C.) such materials prior to adding them with the other metal oxide source materials.

Generally, the metal oxide sources and other additives, if present, are heated to a molten state, and mixed until the melt is homogenous. Typically, the melt is heated to and held at a temperature at least 50° C. (preferably, at least 100° C.) above the melting point of the melt. If the temperature of the melt is too low, the viscosity of the melt may be undesirably too high, making it more difficult to homogenize the various metal oxide sources and other additives making up the melt, or to pour or otherwise transfer the melt from the furnace. If the temperature of the melt is too high temperature, and/or the melt heated for too long, energy will be wasted, and there may be undesirable volatilization of components of the melt as well.

In some cases, it may be desirable, to mix, or otherwise blend the metal oxide sources and other additives (e.g., volatile components (e.g., water or organic solvent) which may assist in forming a homogenous mixture or blend), if present, together prior to forming the melt. For example, particulate metal oxide sources can be milled (e.g., ball milled) to both mix the materials together, as well as reduce the size of the particulate material. Other techniques for mixing or blending the metal oxide sources and other additives, if present, together prior to forming the melt include high shear mixers, paddle mixers, V-blenders, tumblers, and the like. Milling times may range from several minutes to several hours, or even days. Optionally, fugitive materials such as water and organic solvents may be removed from the mixture or blend of metal oxide sources and other additives, for example, by heating, prior to forming the melt. For ease of handling, the metal oxide sources and other additives may also be agglomerated prior to charging them to the furnace.

The atmosphere over the melt may be at atmospheric pressure, a pressure above atmospheric pressure, or a pressure below atmospheric pressure, although a pressure below atmospheric pressure may be preferred in order to reduce the number of pores in the resulting solidified material. The atmosphere over the melt may also be controlled to provide an oxidizing, reducing, or inert atmosphere which may affect the melt chemistry.

Reducing conditions during melting may aid in purifying the melt. In addition to, or alternatively to, adding a reducing agent to the melt, suitable reducing conditions may be obtained using carbon electrodes with an electric arc melting furnace. Under suitable reducing conditions, some impurities (e.g., silica, iron oxide, and titania) will convert to their respective molten metallic form, leading to a higher specific gravity for the melt. Such free metal(s) impurities would then tend to sink to the bottom of the furnace.

In another aspect, it may be desirable to oxidize free metal present in the melt before the melt is cooled (e.g., before pouring the melt from the furnace). For example, an oxygen lance(s) may be inserted into the melt just prior to pouring the melt from the furnace (see, e.g., U.S. Pat. No. 960,712, the disclosure of which is incorporated herein by reference).

The melt can be cooled using any of a variety of techniques known in the art, depending, for example, on the desired article to be formed. In making abrasive particles, for example, the furnace containing the melt is typically capable of being tilted such that the melt can be poured over or into a heat sink. Examples of heat sinks include metallic balls (e.g., cast iron or carbon steel balls), metallic rods, metallic plates, metallic rolls, and the like. In some instances, these heat sink materials may be internally cooled (e.g., water-cooled or a suitable refrigerant) to achieve fast cooling rates. The heat sink material may also be pieces of pre-fused material (having the same or a different composition being solidified) or other refractory material.

Further with regard to heat sinks useful, for example, in making abrasive particles, the melt can be cooled by pouring the melt over and in between a plurality of metallic balls. The balls typically range in diameter from about 1 to 50 cm, more typically 5 to 25 cm. The melt may also be cooled using book molds. Suitable book molds consist of a plurality of thin plates (e.g., metallic or graphite plates) that are spaced relatively close together. The plates are usually spaced less than 10 cm apart, typically less than 5 cm, and preferably less than 1 cm apart. The melt may also be poured into graphite or cast iron molds to form slabs. It is generally preferred that such “slabs” be relatively thin so as to achieve faster cooling rates.

Fibers or rods comprised of fused according to the present invention can be made from the raw materials using techniques and equipment known in the art for making conventional fused fibers. For example, one method for making such fibers is the Czochralski method, wherein a crystal seed is dipped into a melt pool (similar in composition to a seed crystal) and then drawn out of the melt. A variation of this method, is the Edge-defined Film-fed Growth method, which can be used to grow shaped profiles (e.g. tubes, plates) from a thin film of a melt formed under an action of capillary forces. Fibers or rods of different diameters can also be obtained using the Bridgman-Stockbarger method by melting the desired material in a cylindrical crucible and then withdrawing the crucible from a hot zone while carefully controlling the speed and temperature gradients. Zone melting technique and its variation Laser Heated Float Zone (LHFZ) can be used, for example, to make rods.

The cooling rate is believed to affect the microstructure and physical properties of the solidified material, and thus the fused material. Preferably, the melt is rapidly cooled as the size of the crystalline phases of the solidified material generally decreases as the cooling rate increase. Preferred cooling rates are at least 500° C./min.; more preferably, at least 1000° C./min; and even more preferably, at least 1500° C./min. The cooling rate may depend upon several factors including the chemistry of the melt, the melting point of the melt, the type of heat sink, and the heat sink material.

Rapid cooling may also be conducted under controlled atmospheres, such as a reducing, neutral, or oxidizing environment to maintain and/or influence the desired crystalline phases, oxidation states, etc. during cooling.

Additional details on cooling a melt can be found, for example, in U.S. Pat. No. Re 31,128 (Walker et al.), U.S. Pat. No. Re 3,781,172 (Pett et al.), U.S. Pat. No. Re 4,070,796 (Scott et al.), U.S. Pat. No. Re 4,194,887 (Ueltz et al.), U.S. Pat. No. Re 4,415,510 (Richmond), U.S. Pat. No. Re 4,439,845 (Richmond), U.S. Pat. No. Re 5,027,886 (Strom-Olsen et. al), and U.S. Pat. No. Re 5,143,522 (Gibson et al.), the disclosures of which are incorporated herein by reference.

With regard to making abrasive particles, for example, the resulting (solidified) fused material(s) is typically larger in

size than that desired. The fused material can be, and typically is, converted into smaller pieces using crushing and/or comminuting techniques known in the art, including roll crushing, canary milling, jaw crushing, hammer milling, ball milling, jet milling, impact crushing, and the like. In some instances, it is desired to have two or multiple crushing steps. For example, after the molten material is solidified, it may be in the form of a relatively large mass structure (e.g., a diameter greater than 5 cm. The first crushing step may involve crushing these relatively large masses or “chunks” to form smaller pieces. This crushing of these chunks may be accomplished with a hammer mill, impact crusher or jaw crusher. These smaller pieces may then be subsequently crushed to produce the desired particle size distribution. In order to produce the desired particle size distribution (sometimes referred to as grit size or grade), it may be necessary to perform multiple crushing steps. In general the crushing conditions are optimized to achieve the desired particle shape(s) and particle size distribution.

The shape of fused abrasive particles can depend, for example, on the composition and/or microstructure of the abrasive particles, the geometry in which it was cooled, and the manner in which the solidified material is crushed (i.e., the crushing technique used). In general, where a “blocky” shape is preferred, more energy may be employed to achieve this shape. Conversely, where a “sharp” shape is preferred, less energy may be employed to achieve this shape. The crushing technique may also be changed to achieve different desired shapes. Alternatively, abrasive particles may be directly formed into desired shapes by pouring or forming the melt into a mold.

Fused material according to the present invention can be in the form of particles and/or fibers suitable for use as reinforcing materials in composites (e.g., ceramic, metal, or polymeric (thermosetting or thermoplastic). The particles and/or fibers may, for example, increase the modulus, heat resistance, wear resistance, and/or strength of the matrix material. Although the size, shape, and amount of the particles and/or fibers used to make a composite may depend, for example, on the particular matrix material and use of the composite, the size of the reinforcing particles typically range about 0.1 to 1500 micrometers, more typically 1 to 500 micrometers, and preferably between 2 to 100 micrometers. The amount of particles for polymeric applications is typically about 0.5% to about 75% by weight, more typically about 1 to about 50% by weight. Examples of thermosetting polymers include: phenolic, melamine, urea formaldehyde, acrylate, epoxy, urethane polymers, and the like. Examples of thermoplastic polymers include: nylon, polyethylene, polypropylene, polyurethane, polyester, polyamides, and the like.

Examples of uses for reinforced polymeric materials (i.e., reinforcing particles according to the present invention dispersed in a polymer) include protective coatings, for example, for concrete, furniture, floors, roadways, wood, wood-like materials, ceramics, and the like, as well as, anti-skid coatings and injection molded plastic parts and components.

Typically, and preferably, the true density, sometimes referred to as specific gravity, of fused material according to the present invention is typically at least 80% of theoretical density. More preferably, the true density of fused material according to the present invention is at least 85% of theoretical density, even more preferably at least 90% of theoretical density, or even at least 95% of theoretical density.

Typically, fused material according to the present invention have an average hardness (i.e., resistance to deforma-

tion; also referred to as (“microhardness”) of at least 11 GPa; preferably, at least 12, 13, or 14 GPa, more preferably, at least 15 GPa, and even more preferably, at least 16 GPa. In another aspect, fused material according to the present invention typically have an average toughness (i.e., resistance to fracture) of at least 2.0 MPa m^{1/2}; preferably at least 2.5 MPa m^{1/2}, more preferably at least 3.0 MPa m^{1/2}.

Other suitable preparation techniques for making fused material according to the present invention may be apparent to those skilled in the art after reviewing the disclosure herein, as well as, for example, applications having U.S. Ser. Nos. 09,495,978, 09/496,422, 09/496,638, and 09/496,713, each filed on Feb. 2, 2000, and, 09/618,876, 09/618,879, 09/619,106, 09/619,191, 09/619,215, 09/619,289, 09/619,563, 09/619,729, 09/619,744, and 09/620,262, each filed on the same date as the instant application, the disclosure of which are all incorporated herein by reference.

For some fused materials according to the present invention, eutectic phases (e.g., Al₂O₃—Yb₃Al₅O₁₂—ZrO₂) making up the colonies have a lamellar arrangement where one crystalline phase (e.g., alumina crystals) exhibit a trigonal shape. Further, the orientation of at least a portion adjacent lamellars (i.e. orientation of eutectic crystallization) follows the orientation of the trigonal (-shaped phase) outline at an angle of about 120 degrees. While not wishing to be bounded by theory, it is believed that during crystallization of the melt of a composition at or near ternary eutectic, primary crystals of one phase (e.g., alumina) may crystallize first as a seed in a trigonal shape. The consequent coupled growth of eutectic in the form of lamellar follows, at least initially, the orientation of the seed. A eutectic colony then includes seeds (e.g., alumina seeds) of the same orientation (or a single seed) together with the eutectic lamellar growth. Further, colony boundaries may not exhibit phase coarsening as has been observed in binary eutectics (manifested by the significant coarsening of crystals of eutectic phases in an immediate vicinity of colony boundary) such as was observed for Comparative Example A.

Preferred fused material according to the present invention are thermally stable at elevated temperatures, as compared to conventional fused alumina-zirconia materials (including alumina-zirconia abrasive particles available from Norton Company, Worcester, Mass. under the trade designation “NORZON”). When alumina-zirconia eutectic abrasive particles available from Norton Company, Worcester, Mass. under the trade designation “NORZON”, are heated in air, for example, to at least about 350° C., typically at least a portion of the zirconia undergoes a tetragonal and/or cubic to monoclinic phase transformation. This phase transformation is usually detrimental to the structural integrity of the alumina-zirconia material because it involves volume changes to the zirconia crystalline phases. Further, such phase transformations have been observed to occur preferentially at the boundaries of eutectic colonies, which thereby tend to weaken the boundaries, and which in turn tend to lead to significant degradation of mechanical properties (i.e., hardness, strength, etc.) of the material. In addition, various impurities, which are typically segregated during solidification of the melt into the eutectic colonies boundaries may also undergo volumetric structural changes (e.g., due to oxidation), leading to further degradation of mechanical properties (i.e., hardness, strength, etc.) of the material.

By contrast, preferred fused material according to the present invention typically do not exhibit phase transformations of the eutectic phases when heated up to 1000° C. (in

some cases even up to 1400° C.) in air, and thus are thermally stable.

The thermal stability of certain preferred fused material according to the present invention may be measured or illustrated using a variety of different techniques, including: Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA), X-ray diffraction, hardness measurements, microstructure analysis, color change, and interaction with glass bonds. The thermal stability of the fused material may be dependent, for example, upon the composition, particle chemistry, and processing conditions.

In one test for measuring the thermal stability of certain preferred fused material according to the present invention, the average hardness of the fused material is measured before and after being heated in air at 1000° C. in air for 4 hours (see Comparative Example B (below) for a more complete description of the test). Although there may be some degradation of the average microhardness after being heated for 4 hours in air at 1000° C., the average hardness of preferred fused material according to the present invention after being heated for 4 hours in air at 1000° C. are at least 85% (preferably at least 90%, more preferably at least 95%, and even more preferably, about 100% or more) of the average microhardness of the fused material prior to such heating.

The thermal stability of certain preferred fused material according to the present invention may also be observed using Scanning Electron Microscopy (SEM), wherein the average microstructure (e.g., porosity, crystal structure, colony size and crystal size (eutectic crystals, and primary crystals, if present) and integrity of the fused material is examined before and after being heated at 1000° C. in air for 4 hours. The microstructure of certain preferred fused material according to the present invention are essentially the same before and after being heated at 1000° C. in air for 4 hours.

Further, the thermal stability of certain preferred fused material according to the present invention may also be illustrated by comparing the color of the fused material before and after they are heated at 1000° C. in air for 4 hours. The microstructure of certain preferred fused material according to the present invention is essentially the same before and after being heated at 1000° C. in air for 4 hours.

The thermal stability of certain preferred fused material according to the present invention may also be illustrated by comparing powder XRD result of the fused material before and after they are heated at 1000° C. in air for 4 hours. As discussed above, when alumina-zirconia eutectic material is heated in air, typically at least a portion of the zirconia undergoes a tetragonal and/or cubic to monoclinic phase transformation. The effect of this phase transformation is typically significant enough to be observed via powder XRD. By contrast, the eutectic phases of certain preferred fused material according to the present invention do not exhibit such phase transformations when heated to 1000° C. in air, hence no such transformation of the eutectic phases will be observed in the XRD results.

Fused material according to the present invention can be used in conventional abrasive products, such as coated abrasive products, bonded abrasive products (including vitrified, resinoid, and metal bonded grinding wheels, cutoff wheels, mounted points, and honing stones), nonwoven abrasive products, and abrasive brushes. Typically, abrasive products (i.e., abrasive articles) include binder and abrasive particles, at least a portion of which is fused abrasive particles according to the present invention, secured within the abrasive product by the binder. Methods of making such

abrasive products and using abrasive products are well known to those skilled in the art (see, e.g., U.S. Pat. No. 5,427,595 (Pihl et al.), U.S. Pat. No. 5,443,906 (Pihl et al.), U.S. Pat. No. 5,679,067 (Johnson et al.), U.S. Pat. No. 5,903,951 (Ionta et al.) U.S. Pat. No. 4,588,419 (Caul et al.), U.S. Pat. No. 4,751,137 (Tumey et al.), U.S. Pat. No. 5,436,063 (Follett et al.), U.S. Pat. No. 4,314,827 (Leitheiser et al.), U.S. Pat. No. 4,518,397 (Leitheiser et al.), U.S. Pat. No. 4,623,364 (Cottringer et al.), U.S. Pat. No. 4,744,802 (Schwabel), U.S. Pat. No. 4,770,671 (Monroe et al.), U.S. Pat. No. 4,881,951 (Wood et al.), U.S. Pat. No. 5,011,508 (Wald et al.), U.S. Pat. No. 5,090,968 (Pellow), U.S. Pat. No. 5,139,978 (Wood), U.S. Pat. No. 5,201,916 (Berg et al.), 5,227,104 (Bauer), U.S. Pat. No. 5,366,523 (Rowenhorst et al.), U.S. Pat. No. 5,429,647 (Larmie), U.S. Pat. No. 5,498,269 (Larmie), U.S. Pat. No. 5,551,963 (Larmie), U.S. Pat. No. 4,311,489 (Kressner), U.S. Pat. No. 4,652,275 (Bloecher et al.), U.S. Pat. No. 4,799,939 (Bloecher et al.), U.S. Pat. No. 5,549,962 (Holmes et al.), and U.S. Pat. No. 5,975,988 (Christianson), U.S. Pat. No. 4,734,104 (Broberg), U.S. Pat. No. 4,737,163 (Larkey), U.S. Pat. No. 5,203,884 (Buchanan et al.), U.S. Pat. No. 5,152,917 (Pieper et al.), U.S. Pat. No. 5,378,251 (Culler et al.), U.S. Pat. No. 5,417,726 (Stout et al.), U.S. Pat. No. 5,436,063 (Follett et al.), U.S. Pat. No. 5,496,386 (Broberg et al.), U.S. Pat. No. 5,609,706 (Benedict et al.), U.S. Pat. No. 5,520,711 (Helmin), U.S. Pat. No. 5,954,844 (Law et al.), U.S. Pat. No. 5,961,674 (Gagliardi et al.), U.S. Pat. No. 4,543,107 (Rue), U.S. Pat. No. 4,741,743 (Narayanan et al.), U.S. Pat. No. 4,800,685 (Haynes et al.), U.S. Pat. No. 4,898,597 (Hay et al.), U.S. Pat. No. 4,997,461 (Markhoff-Matheny et al.), U.S. Pat. No. 5,038,453 (Narayanan et al.), U.S. Pat. No. 5,110,332 (Narayanan et al.), U.S. Pat. No. 5,863,308 (Qi et al.), U.S. Pat. No. 5,094,672 (Giles et al.), U.S. Pat. No. 5,118,326 (Sheldon et al.), U.S. Pat. No. 5,131,926 (Sheldon et al.), U.S. Pat. No. 5,203,886 (Sheldon et al.), U.S. Pat. No. 5,282,875 (Wood et al.), 5,738,696 (Wu et al.), U.S. Pat. No. 5,863,308 (Qi), and U.S. Pat. No. 2,958,593 (Hoover et al.), the disclosure of which is incorporated herein by reference). Furthermore, fused abrasive particles according to the present invention can be used in abrasive applications that utilize loose abrasive particles, such as slurries of abrading compounds (e.g., polishing compounds), milling media, shot blast media, vibratory mill media, and the like.

EXAMPLES

This invention is further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. Various modifications and alterations of the present invention will become apparent to those skilled in the art. All parts and percentages are by weight unless otherwise indicated.

Comparative Example A

A polyethylene bottle was charged with 242.5 grams of alumina powder (obtained under the trade designation "APA-0.5" from Condea Vista, Tucson, Ariz.), 257.5 grams of gadolinium oxide powder (obtained from Molycorp, Inc., Brea, Calif.), 0.6 gram of a dispersing agent (obtained under the trade designation "DURAMAX D-30005" from Rohm and Haas Company, Dear Park, Tex.), and 150.6 grams of distilled water. The powders were present in amounts to provide 77 mole % Al_2O_3 and 23 mole % Gd_2O_3 . About 450 grams of alumina milling media (10 mm diameter; 99.9%

alumina; obtained from Union Process, Akron, Ohio) were added to the bottle, and the mixture was milled for 4 hours to thoroughly mix the ingredients. After the milling, the milling media were removed and the slurry was poured onto a glass ("PYREX") pan where it was dried using a heat-gun held approximately 46 cm (18 inches) above the pan. The pan was slowly oscillated while drying to prevent the settling of the powder prior to complete drying. After drying with the heat-gun, the pan was placed in a drying oven for an additional 30 minutes at 90° C. to more completely dry the material. The dried powder bed was then scored with a spatula and scraped from the pans to form small flakes of material. Each flake weighed about 0.5 to 3 grams. The flakes were calcined in air by heating them to 600° C. at rate of about 1° C./min, and then holding them at 600° C. for 1 hour, after which the power to the furnace power was shut-off, and the furnace allowed to cool back to room temperature.

Several of the calcined flakes were melted in an arc discharge furnace (Model No. 1-VAMF-20-22-45; from Advanced Vacuum Systems, Ayer, Mass.). About 15 grams of the calcined flakes were placed on the chilled copper plate located inside a furnace chamber. The furnace chamber was evacuated and then backfilled with Argon gas at a 260 torr pressure. An arc was struck between an electrode and a plate. The temperatures generated by the arc discharge were high enough to quickly melt the calcined flakes. After melting was complete, the material was maintained in a molten state for about 30 seconds to homogenize the melt. The resultant melt was rapidly cooled by shutting off the arc and allowing the melt to cool on its own. Rapid cooling was ensured by the small mass of the sample and the large heat sinking capability of the water chilled copper plate. The fused material was removed from the furnace within one minute after the power to the furnace was turned off. Although not wanting to be bound by theory, it is estimated that the cooling rate of the melt on the surface of the water chilled copper plate was 1500° C./min. The fused material was white-yellow in color.

FIG. 5 is a scanning electron microscope (SEM) photomicrograph of a polished section of fused Comparative Example A material. The polished section was prepared using conventional mounting and polishing techniques. Polishing was done using a polisher (obtained from Buehler of Lake Bluff, Ill. under the trade designation "ECOMET 3 TYPE POLISHER-GRINDER"). The sample was polished for about 3 minutes with a diamond wheel, followed by three minutes of polishing with each of 45, 30, 15, 9, and 3 micrometer diamond slurries. The polished sample was coated with a thin layer of gold-palladium and viewed using JEOL SEM (Model JSM 840A). Referring again to FIG. 5, the photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 5–20 micrometers in size. Based on powder x-ray diffraction of a portion of Comparative Example A material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline GdAlO₃, and the dark portions α-Al₂O₃. The widths of these phases observed in the polished section were up to about 0.7 micrometer. It is also noted that there were many pores observed in the fused material.

Comparative Example A fused material was crushed by using a "Chipmunk" jaw crusher (Type VD; manufactured by BICO Inc., Burbank, Calif.) into (abrasive) particles and graded to retain the -25+30 and -30+35 mesh fractions (USA Standard Testing Sieves). These two mesh fractions

were combined to provide a 50/50 blend. Thirty grams of the 50/50 blend of -25+30 and -30+35 mesh fractions were incorporated into a coated abrasive disc. The coated abrasive disc was made according to conventional procedures. The fused abrasive particles were bonded to 17.8 cm diameter, 0.8 mm thick vulcanized fiber backings (having a 2.2 cm diameter center hole) using a conventional calcium carbonate-filled phenolic make resin (48% resole phenolic resin, 52% calcium carbonate, diluted to 81% solids with water and glycol ether) and a conventional cryolite-filled phenolic size resin (32% resole phenolic resin, 2% iron oxide, 66% cryolite, diluted to 78% solids with water and glycol ether). The wet make resin weight was about 185 g/m². Immediately after the make coat was applied, the fused abrasive particles were electrostatically coated. The make resin was precured for 120 minutes at 88° C. Then the cryolite-filled phenolic size coat was coated over the make coat and abrasive particles. The wet size weight was about 850 g/m². The size resin was cured for 12 hours at 99° C. The coated abrasive disc was flexed prior to testing.

Comparative Example B

Comparative Example B fused material, abrasive particles, and discs were prepared as described in Comparative Example A, except (a) the polyethylene bottle was charged with 145.6 grams of alumina powder ("APA-0.5"), 151.2 grams of lanthanum oxide powder (obtained from Molycorp, Inc., Brea, Calif.), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 129.5 grams of distilled water, and (b) the powders were present in amounts to provide 75 mole % Al₂O₃ and 25 mole % La₂O₃. The fused material was white-red in color; although some of the abrasive particles were redder than others.

FIG. 6 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Comparative Example B material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 5–30 micrometers in size. Based on powder x-ray diffraction of a portion of Comparative Example B material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline LaAlO₃, and the dark portions crystalline LaAl₁₁O₁₈. The widths of these phases observed in the polished section were up to about 0.5 micrometer. Further, large primary crystals (believed to be LaAlO₃), present in the form of dendrites, were observed in some areas of the polished cross-section, indicating possible deviation of the composition from an exact eutectic composition toward a La₂O₃ rich composition.

The average microhardness of Comparative Example B abrasive particles were measured by mounting loose Comparative Example B abrasive particles (together with Comparative Example C and D abrasive particles) (about 10 mesh in size) in mounting resin (obtained under the trade designation "EPOMET" from Buehler Ltd., Lake Bluff, Ill.). The resulting cylinder of resin was about 2.5 cm (1 inch) in diameter and about 1.9 cm (0.75 inch) tall. The mounted samples were polished using a conventional grinder/polisher (obtained under the trade designation "EPOMET" from Buehler Ltd.) and conventional diamond slurries with the final polishing step using a 1 micrometer diamond slurry (obtained under the trade designation "METADI" from Buehler Ltd.) to obtain polished cross-sections of the sample.

The microhardness measurements were made using a conventional microhardness tester (obtained under the trade

designation "MITUTOYO MVK-VL" from Mitutoyo Corporation, Tokyo, Japan) fitted with a Vickers indenter using a 500-gram indent load. The microhardness measurements were made according to the guidelines stated in ASTM Test Method E384 Test Methods for Microhardness of Materials (1991), the disclosure of which is incorporated herein by reference. The microhardness values were an average of 20 measurements. The average microhardness was 15.0 GPa.

Several Comparative Example B abrasive particles (together with Comparative Example C and D abrasive particles) were heated placed in a platinum crucible and heated to 1000° C. at 50° C./hour, held at 1000° C. for 4 hours (in air), and then cooled to room temperature at about 100° C./hour. The color of the Comparative Example B abrasive particles after heating was the same as before heating (i.e., white-red). The average microhardness of the Comparative Example B abrasive particles after heating was 14.1 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed for the Comparative Example B abrasive particles after heating was substantially the same as the microstructure observed before heating.

Several Comparative Example B abrasive particles (together with Comparative Example C and D abrasive particles) were also heated placed in a platinum crucible and heated to 1000° C. at 50° C./hour, held at 1000° C. for 8 hours (in air), and then cooled to room temperature at about 100° C./hour. The color of the Comparative Example B abrasive particles after heating was the same as before heating (i.e., white-red). The average microhardness of the Comparative Example B abrasive particles after heating was 14.3 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed for the Comparative Example B abrasive particles after heating was substantially the same as the microstructure observed before heating.

The effect of two vitrified bonding materials on Comparative Example B abrasive particles were evaluated as follows. A first vitrified bond material was prepared by charging a plastic jar (4 3/8 inches (11.1 cm) in diameter; 4 3/8 inches (11.1 cm) in height) with 70 parts of a glass flit (37.9% SiO₂, 28.5% B₂O₃, 15.6% Al₂O₃, 13.9% Na₂O, and 4.1% K₂O; obtained under the trade designation "FERRO FRIT 3227" from Ferro Corporation, Cleveland, Ohio), 27 parts of Kentucky Ball Clay (No 6DC; obtained from Old Hickory Clay Company, Hickory, Ky.), 3.5 parts of Li₂CO₃ (obtained from Alfa Aesar Chemical Company, Ward Hill, Mass.), 3 parts CaSiO₃ (obtained from Alfa Aesar Chemical Company), and 625 grams of 1.3 cm (0.5 inch) diameter plastic coated steel media, and then dry milling the contents at 90 rpm for 7 hours. The composition was formulated to provide a vitrified bond material comprising about 45% SiO₂, about 19% Al₂O₃, about 20% B₂O₃, about 10% Na₂O, about 3% K₂O, about 1.5% Li₂O, and about 1.5% CaO. The dry milled material and Example 2 abrasive particles (and Example 3 and 4 abrasive particles) were pressed into a 3.2 cm×0.6 cm (1.25 inch×0.25 inch) pellet. The pellet was heated to 1000° C. at 50° C./hour, held at 1000° C. for 8 hours (in air), and then cooled to room temperature at about 100° C./hour. The pellet was prepared by mixing, in order, 26 parts of Comparative Example B, C, and D abrasive particles (i.e., Comparative Example B, C, and D abrasive particles were mixed together; but were distinguishable from each other visually based on color, and under SEM based on

composition) (-20+30 mesh), 0.24 part of hydrolyzed starch (obtained under the trade designation "DEXTRIN" from Aldrich Chemical Company, Milwaukee, Wis.), 0.02 part glycerine (obtained from Aldrich Chemical Company), 0.72 part water, 3.14 parts of the dry milled material, and 0.4 part of hydrolyzed starch ("DEXTRIN"). The pellet was pressed under a load of 2273 kilograms (5000 lbs.). A polished cross-section prepared as described above for microhardness measurements, were examined using the SEM in the secondary electron mode. The microstructure observed after heating was substantially the same as the microstructure observed before heating. The color of the Comparative Example B abrasive particles after heating with the vitrified bonding material was the same as before heating (i.e., white-red).

A second vitrified bond material was prepared by charging a plastic jar (4 3/8 inches (11.1 cm) in diameter; 4 3/8 inches (11.1 cm) in height) with 45 parts of Kentucky Ball Clay (No. 6DC; obtained from Old Hickory Clay Company), 28 parts of anhydrous sodium tetraborate (obtained from Alfa Aesar Chemical Company), 25 parts of feldspar (obtained under the trade designation "G-200 Feldspar" from Feldspar Corporation, Atlanta, Ga.), 3.5 parts of Li₂CO₃ (obtained from Alfa Aesar Chemical Company), 2.5 parts of CaSiO₃ (obtained from Alfa Aesar Chemical Company), and 625 grams of 1.3 cm (0.5 inch) diameter plastic coated steel media, and then dry milling the contents at 90 rpm for 7 hours. The composition was formulated to provide a vitrified bond material comprising about 45% SiO₂, about 19% Al₂O₃, about 20% B₂O₃, about 10% Na₂O, about 3% K₂O, about 1.5% Li₂O, and about 1.5% CaO. The dry milled material and Comparative Example B abrasive particles were pressed into a 3.2 cm×0.6 cm (1.25 inch×0.25 inch) pellet). The pellet was heated to 1000° C. at 50° C./hour, held at 1000° C. for 8 hours (in air), and then cooled to room temperature at about 100° C./hour. The pellet was prepared by mixing, in order, 26 parts of Comparative Example B, C, and D abrasive particles (i.e., Comparative Example B, C, and D abrasive particles were mixed together (-20+30 mesh, 0.24 part of hydrolyzed starch ("DEXTRIN"), 0.02 part glycerine (obtained from Aldrich Chemical Company), 0.72 part water, 3.14 parts of the dry milled material, and 0.4 part of hydrolyzed starch ("DEXTRIN"). The pellet was pressed under a load of 2273 kilograms (5000 lbs.). A polished cross-section prepared as described above for microhardness measurements, were examined using the SEM in the secondary electron mode. The microstructure observed after heating was substantially the same as the microstructure observed before heating. The color of the Comparative Example B abrasive particles after heating with the vitrified bonding material was the same as before heating (i.e., white-red).

Comparative Example C

Comparative Example C fused material, abrasive particles, and discs were prepared as described in Comparative Example A, except (a) the polyethylene bottle was charged with 143.6 grams of alumina powder ("APA-0.5"), 147.6 grams of neodymium oxide powder (obtained from Molycorp, Inc., Brea, Calif.), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 138.5 grams of distilled water, and (b) the powders were present in amounts to provide 75 mole % Al₂O₃ and 25 mole % Nd₂O₃. The fused material was white-blue in color; although some of the abrasive particles were bluer than others.

FIG. 7 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in

Comparative Example A) of fused Comparative Example C material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 10–40 micrometers in size. Based on powder x-ray diffraction of a portion of Comparative Example C material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline NdAlO_3 , and the dark portions crystalline $\text{NdAl}_{11}\text{O}_{18}$. The widths of these phases observed in the polished section were up to about 0.5 micrometer. Further, large primary crystals (believed to be NdAlO_3), present in the form of dendrites, were observed in some areas of the polished cross-section, indicating possible deviation of the composition from an exact eutectic composition toward a Nd_2O_3 rich composition.

The average microhardness of Comparative Example C abrasive particles was determined, as described above in Comparative Example B, to be 14.5 GPa.

Several Comparative Example C abrasive particles (together with Comparative Example B and D abrasive particles) were heated placed in a platinum crucible and heated to 1000° C. at 50° C./hour, held at 1000° C. for 4 hours (in air), and then cooled to room temperature at about 100° C./hour. The color of the Comparative Example C abrasive particles after heating was the same as before heating (i.e., white-blue). The average microhardness of the Comparative Example C abrasive particles after heating was 14.1 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed for the Comparative Example C abrasive particles after heating was substantially the same as the microstructure observed before heating.

Several Comparative Example C abrasive particles (together with Comparative Example B and D abrasive particles) were also heated placed in a platinum crucible and heated to 1000° C. at 50° C./hour, held at 1000° C. for 8 hours (in air), and then cooled to room temperature at about 100° C./hour. The color of the Comparative Example C abrasive particles after heating was the same as before heating (i.e., white-blue). The average microhardness of the Comparative Example C abrasive particles after heating was 14.5 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed for the Comparative Example C abrasive particles after heating was substantially the same as the microstructure observed before heating.

The effect of two vitrified bonding materials on Comparative Example C abrasive particles were evaluated as described in Comparative Example B. The polished cross-sections were examined using the SEM in the secondary electron mode. The microstructure observed after heating was substantially the same as the microstructure observed before heating. The color of the Comparative Example C abrasive particles after heating with the vitrified bonding material was the same as before heating (i.e., white-blue).

Comparative Example D

A lanthanum carbonate powder (obtained from Aptech Services, LLC, Houston, Tex.; Lot No.: SH99-5-7) was heated to 900° C. to convert it to lanthanum oxide and some cerium (IV) oxide (manufacturer's conversion specifications were 95% La_2O_3 and 4.19% CeO_2 , with a carbonate to oxide yield of 49.85 wt. % metal oxide). Comparative Example D

fused material, abrasive particles, and discs were prepared as described in Comparative Example A, except (a) the polyethylene bottle was charged with 148.6 grams of the lanthanum/cerium oxide powder, 146.4 grams of alumina powder ("APA-0.5"), 0.6 gram of a dispersing agent ("DURAMAX D-30005") and 141.3 grams of distilled water, and (b) the powders were present in amounts to provide 75 mole % Al_2O_3 and 25 mole % $\text{La}_2\text{O}_3/\text{Ce}_2\text{O}_3$. It was observed that the slurry was significantly more viscous as compared to the slurry of Comparative Example B. The fused material was bright orange in color.

FIG. 8 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example B) of fused Comparative Example D material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 5–25 micrometers in size. Based on powder x-ray diffraction of a portion of Comparative Example D material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline LaAlO_3 , and the dark portions crystalline $\text{LaAl}_{11}\text{O}_{18}$. The widths of these phases observed in the polished section were up to about 0.5 micrometer. Further, large primary crystals (believed to be LaAlO_3), present in the form of dendrites, were observed in some areas of the polished cross-section, indicating possible deviation of the composition from an exact eutectic composition toward a La_2O_3 rich composition.

The average microhardness of Comparative Example D abrasive particles was determined, as described above in Comparative Example B, to be 14.8 GPa.

Several Comparative Example D abrasive particles (together with Comparative Example B and C abrasive particles) were heated placed in a platinum crucible and heated to 1000° C. at 50° C./hour, held at 1000° C. for 4 hours (in air), and then cooled to room temperature at about 100° C./hour. The color of the Comparative Example D abrasive particles after heating was the same as before heating (i.e., bright orange). The average microhardness of the Comparative Example D abrasive particles after heating was 14.7 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed for the Comparative Example D abrasive particles after heating was substantially the same as the microstructure observed before heating.

Several Comparative Example D abrasive particles (together with Comparative Example B and C abrasive particles) were also heated placed in a platinum crucible and heated to 1000° C. at 50° C./hour, held at 1000° C. for 8 hours (in air), and then cooled to room temperature at about 100° C./hour. The color of the Comparative Example D abrasive particles after heating was the same as before heating (i.e., bright orange). The average microhardness of the Comparative Example D abrasive particles after heating was 14.1 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed for the Comparative Example D abrasive particles after heating was substantially the same as the microstructure observed before heating.

The effect of two vitrified bonding materials on Comparative Example D abrasive particles were evaluated as described in Comparative Example B. The polished cross-sections were examined using the SEM in the secondary

electron mode. The microstructure observed after heating was substantially the same as the microstructure observed before heating. The average microhardness of the Comparative Example D abrasive particles after heating in the two vitrified bonding materials was 14.2 GPa and 14.3 GPa, respectively. The color of the Comparative Example D abrasive particles after heating with each of the two vitrified bonding materials was the same as before heating (i.e., bright orange).

Comparative Example E

The Comparative Example E coated abrasive disc was prepared as described in Comparative example A except heat-treated fused alumina abrasive particles (obtained under the trade designation "ALODUR BFRPL" from Triebacher, Villach, Austria) was used in place of the Comparative Example A fused abrasive particles.

Comparative Example F

The Comparative Example F coated abrasive disc was prepared as described in Comparative Example A except alumina-zirconia abrasive particles (having a eutectic composition of 53% Al₂O₃ and 47% ZrO₂; obtained under the trade designation "NORZON" from Norton Company, Worcester, Mass.) was used in place of the Comparative Example A fused abrasive particles.

The average microhardness of Comparative Example F abrasive particles was determined, as described above in Comparative Example B, to be 16.0 GPa. The color of the Comparative Example F abrasive particles was gray-navy blue.

Several Comparative Example F abrasive particles were heated placed in a platinum crucible and heated to 1000° C. at 50° C./hour, held at 1000° C. for 4 hours (in air), and then cooled to room temperature at about 100° C./hour. The color of the abrasive particles after heating was beige. The average microhardness of the abrasive particles after heating was 12.9 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. An SEM photomicrograph a Comparative Example F abrasive particle before heating is shown in FIG. 13. An SEM photomicrograph a Comparative Example F abrasive particle after heating is shown in FIG. 14. The microstructure observed after heating was different than that observed before heating. The differences were observed most predominately at the colony boundaries.

Further powder x-ray diffraction (using a Phillips XRG 3100 x-ray diffractometer with copper K α 1 radiation of 1.54050 Angstrom) was used to qualitatively measure the phases present in Comparative Example F abrasive particles before and after the above described heat-treatment by comparing the peak intensities of 111 of cubic and/or tetragonal reflection at about $2\theta=30$ degrees, to that of 111 of monoclinic reflection at about $2\theta=28$ degrees. For reference see "Phase Analysis in Zirconia Systems," Garvie, R. C. and Nicholson, P. S., Journal of the American Ceramic Society, vol 55 (6), pp. 303-305, 1972, the disclosure of which is incorporated herein by reference. The samples were ground and -120 mesh powders used for analysis. The unheat-treated Comparative Example F abrasive particles contained both the monoclinic and cubic and/or tetragonal zirconia phases. For the heat-treated sample, a decrease in the cubic and/or tetragonal phase content with a corresponding increase in monoclinic phase content was observed.

Several Comparative Example F abrasive particles were heated placed in a platinum crucible and heated to 1000° C.

at 50° C./hour, held at 1000° C. for 8 hours (in air), and then cooled to room temperature at about 100° C./hour. The color of the abrasive particles after heating was beige. The average microhardness of the abrasive particles after heating was 12.8 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. An SEM photomicrograph a Comparative Example F abrasive particle after heating is shown in FIG. 15. The microstructure observed after heating was different than that observed before heating. The differences, which were greater than those observed for the heat-treatment at 1000° C. for 4 hours, were again observed most predominately at the colony boundaries.

The effect of two vitrified bonding materials on Comparative Example F abrasive particles were evaluated as described in Comparative Example B, except 20 parts of Comparative Example F abrasive particles (-20+30 mesh) rather than 26 parts. The average microhardness of the abrasive particles after heating in the first vitrified bonding material was 13.6 GPa, although some of the Comparative example F abrasive particles exhibit such severe degradation that microhardness measurements could not be effectively made (portions of the particles were too weak). There was variability in the color of the heat-treated abrasive particles, although the majority of the particles were beige. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. An SEM photomicrograph a Comparative Example F abrasive particle after heating is shown in FIG. 16. The microstructure observed after heating was different than that observed before heating. The differences, which were greater than those observed for the heat-treatment at 1000° C. for 4 hours, were again observed most predominately at the colony boundaries.

The average microhardness of the abrasive particles after heating in the second vitrified bonding material was 13.4 GPa, although some of the Comparative Example F abrasive particles exhibit such severe degradation that microhardness measurements could not be effectively made (portions of the particles were too weak). There was variability in the color of the heat-treated abrasive particles, although the majority of the particles were beige. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed after heating was different than that observed before heating. The differences, which were greater than those observed for the heat-treatment at 1000° C. for 4 hours, were again observed most predominately at the colony boundaries.

Comparative Example G

The Comparative Example G coated abrasive disc was prepared as described in Comparative Example A except sol-gel-derived abrasive particles (commercially available under the trade designation "321 CUBITRON" from the 3M Company, St. Paul, Minn.) was used in place of the Comparative Example A fused abrasive particles.

Grinding Performance of Comparative Examples A-G

The grinding performance of Comparative Examples A-G coated abrasive discs were evaluated as follows. Each coated abrasive disc was mounted on a beveled aluminum back-up pad, and used to grind the face of a pre-weighed 1.25 cm×18 cm×10 cm 1018 mild steel workpiece. The disc was driven at 5,000 rpm while the portion of the disc

overlaying the beveled edge of the back-up pad contacted the workpiece at a load of 8.6 kilograms. Each disc was used to grind individual workpiece in sequence for one-minute intervals. The total cut was the sum of the amount of material removed from the workpieces throughout the test period. The total cut by each sample after 12 minutes of grinding as well as the cut at 12th minute (i.e., the final cut) are reported in Table 1 below.

TABLE 1

Example	Total cut, g	Final cut, g
Comp. A	732	56
Comp. B	585	41
Comp. C	603	37
Comp. D	564	34
Comp. E	418	23
Comp. F	621	48
Comp. G	859	75

Comparative Example H

Comparative Example H fused material and abrasive particles were prepared as described in Comparative Example A, except (a) the polyethylene bottle was charged with 144.5 grams of alumina powder ("APA-0.5"), 147.4 grams of cerium (IV) oxide (CeO_2) powder, (obtained from Aldrich Chemical Company, Inc.), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 137.5 grams of distilled water, (b) the powders were present in amounts to provide 75 mole % Al_2O_3 and 25 mole % Ce_2O_3 . The fused material was intense yellow-green in color.

FIG. 9 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Comparative Example H material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 5–30 micrometers in size. Based on powder x-ray diffraction of a portion of Comparative Example H material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline CeAlO_3 and crystalline CeO_2 , and the dark portions crystalline $\text{CeAl}_{11}\text{O}_{18}$. The widths of these phases observed in the polished section were up to about 0.5 micrometer. Further, large primary crystals (believed to be CeAlO_3 and/or CeO_2), present in the form of dendrites, were observed in some areas of the polished cross-section, indicating possible deviation of the composition from an exact eutectic composition toward a CeAlO_3 and/or CeO_2 rich composition.

Comparative Example I

Comparative Example I fused material and abrasive particles were prepared as described in Comparative Example A, except (a) the polyethylene bottle was charged with 146.5 grams of alumina powder ("APA-0.5"), 147.4 grams of dysprosium oxide powder (obtained from Aldrich Chemical Company, Inc.), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 136.3 grams of distilled water, and (b) the powders were present in amounts to provide 78 mole % Al_2O_3 and 22 mole % Dy_2O_3 . The fused material was white in color.

FIG. 10 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Comparative Example I material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colo-

nies were about 5–20 micrometers in size. Based on powder x-ray diffraction of a portion of Comparative Example I material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline $\text{Dy}_3\text{Al}_5\text{O}_{12}$, and the dark portions $\alpha\text{-Al}_2\text{O}_3$. The widths of these phases observed in the polished section were up to about 1 micrometer. Primary crystals were not observed.

Comparative Example J

Comparative Example J fused material and abrasive particles were prepared as described in Comparative Example A, except (a) the polyethylene bottle was charged with 146.3 grams of alumina powder ("APA-0.5"), 148.4 grams of ytterbium oxide powder (obtained from Aldrich Chemical Company, Inc.), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 139.6 grams of distilled water, (b) the powders were present in amounts to provide 78.6 mole % Al_2O_3 and 21.4 mole % Yb_2O_3 . The fused material was gray in color.

FIG. 11 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Comparative Example J material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies are about 5–25 micrometers in size. Based on powder x-ray diffraction of a portion of Comparative Example J material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline $\text{Yb}_3\text{Al}_5\text{O}_{12}$, and the dark portions $\alpha\text{-Al}_2\text{O}_3$. The width of these phases observed in the polished section were up to about 1 micrometer. Further, large primary crystals (believed to be $\alpha\text{-Al}_2\text{O}_3$), present in the form of dendrites, were observed in some areas of the polished cross-section, indicating possible deviation of the composition from an exact eutectic composition toward an Al_2O_3 rich composition.

Comparative Example K

Comparative Example K fused material and abrasive particles were prepared as described in Comparative Example A, except (a) the polyethylene bottle was charged with 149.5 grams of alumina powder ("APA-0.5"), 149.4 grams of yttria-stabilized zirconia oxide powder (with a nominal composition of 94 wt % ZrO_2 (+ HfO_2) and 5.4 wt % Y_2O_3 ; obtained under the trade designation "HSY 3.0" from Zirconia Sales, Inc. of Marietta, Ga.), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 136.5 grams of distilled water, and (b) the powders were present in amounts to provide 54.8 mole % Al_2O_3 and 45.2 mole % ZrO_2 . The fused material was white in color.

FIG. 12 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Comparative Example K material. The photomicrograph shows a eutectic derived microstructure comprising a plurality of colonies. The colonies were about 5–40 micrometers in size. Based on powder x-ray diffraction of a portion of Comparative Example K material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline ZrO_2 , and the dark portions $\alpha\text{-Al}_2\text{O}_3$. The widths of these phases observed in the polished section were up to about 0.5 micrometer.

The average microhardness of Comparative Example K was determined, as described above in Comparative Example B, to be 15.3 GPa.

Several Comparative Example K particles were heated placed in a platinum crucible and heated to 1000° C. at 50° C./hour, held at 1000° C. for 4 hours (in air), and then cooled to room temperature at about 100° C./hour. The color of the abrasive particles after heating was white. The average microhardness of the abrasive particles after heating was 15.0 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. An SEM photomicrograph Comparative Example K material before heating is shown in FIG. 17. The microstructure observed after heating was substantially the same as the microstructure observed before heating.

Further powder x-ray diffraction, as described above for Comparative Example F, was used to qualitatively measure the phases present in Comparative Example K material before and after the above described heat-treatment by comparing the peak intensities of 111 of cubic and/or tetragonal reflection at about $2\theta=30$ degrees, to that of 111 of monoclinic reflection at about $2\theta=28$ degrees. The unheat-treated Comparative Example K material contained predominantly cubic and/or tetragonal zirconia before and after the heat-treatment (i.e., there was no significant difference noted in the x-ray diffraction results).

Several Comparative Example K particles were also heated placed in a platinum crucible and heated to 1000° C. at 50° C./hour, held at 1000° C. for 8 hours (in air), and then cooled to room temperature at about 100° C./hour. The color of the abrasive particles after heating was white. The average microhardness of the abrasive particles after heating was 15.0 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed after heating was only slightly different than that observed before heating. An SEM photomicrograph Comparative Example K after heating is shown in FIG. 18. There was some cracks observed in the heat-treated material, generally near primary crystals of ZrO₂.

Differential Thermal Analysis (DTA) And Thermogravimetric Analysis (TGA) of Comparative Examples B, C, F, and K Abrasive Particles/ Materials

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were conducted for each of Comparative Examples B, C, F, and K abrasive particles/materials. Each material was crushed with a mortar and pestle and screened to retain particles that were in the 400–500 micrometer size range.

DTA/TGA runs were made (using an instrument obtained from Netzsch Instruments, Selb, Germany under the trade designation “NETZSCH STA 409 DTA/TGA”) for each of the screened samples. The amount of each screened sample placed in the 100 microliter Al₂O₃ sample holder was 127.9 micrograms (Comparative Examples B), 125.8 micrograms (Comparative Example KI), 127.3 micrograms (Comparative Example B), respectively. Each sample was heated in static air at a rate of 10° C./minute from room temperature (about 25° C.) to 1300° C.

Referring to FIG. 1, line 167 is the plotted DTA data for the Comparative Example B material; line 169, the plotted TGA data. Referring to FIG. 2, line 197 is the plotted DTA data for the Comparative Example C material; line 199, the plotted TGA data. Referring to FIG. 3, line 177 is the plotted DTA data for the Comparative Example K material; line 179, the plotted TGA data. Referring to FIG. 4, line 187 is

the plotted DTA data for the Comparative Example F material; line 189, the plotted TGA data. The change in weight of the sample through the TGA run was, for Comparative Example B, 0.22%; for Comparative Example C, 0.22%; for Comparative Example K, 0.73%; and, for Comparative Example F, 1.16%.

Example 1

Example 1 fused material and abrasive particles were prepared as described in Comparative Example A, except the polyethylene bottle was charged with 122.4 grams of alumina powder (“APA-0.5”), 132.6 grams of ytterbium oxide powder (obtained from Aldrich Chemical Company, Inc.) in place of the gadolinium oxide powder, 45 grams of zirconium oxide powder (with a nominal composition of 100 wt % ZrO₂ (+HfO₂); obtained under the trade designation “DK-2” from Zirconia Sales, Inc. of Marietta, Ga.), 0.6 gram of a dispersing agent (“DURAMAX D-30005”), and 140.2 grams of distilled water. The fused material was white-gray in color.

FIG. 19 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Example 1 material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 5–25 micrometers in size. Based on powder x-ray diffraction of a portion of Example 1 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline Yb₃Al₅O₁₂, and the dark portions crystalline α -Al₂O₃. The shape of ZrO₂ crystallites was not easily discerned on the photomicrograph. The widths of these phases observed in the polished section were up to about 1 micrometer.

Example 2

Example 2 fused material, abrasive particles, and discs were prepared as described in Comparative Example A, except a polyethylene bottle was charged with 127.25 grams of alumina powder (“APA-0.5”), 127.75 grams of gadolinium oxide powder (obtained from Molycorp, Inc.), 45 grams of zirconium oxide powder (“DK-2”), 0.6 gram of a dispersing agent (“DURAMAX D-30005”), and 150 grams of distilled water.

FIG. 20 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Example 2 material. The photomicrograph shows a eutectic-derived microstructure. Based on powder x-ray diffraction of a portion of Example 2 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline GdAlO₃, and the dark portions α -Al₂O₃. The shape of ZrO₂ crystallites was not easily discerned on the photomicrograph. The width of the crystals of phases observed in the polished section were up to about 1 micrometer.

Example 3

Example 3 fused material and abrasive particles were prepared as described in Comparative Example A except the polyethylene bottle was charged with 124.5 grams of alumina powder (“APA-0.5”), 125.3 grams of dysprosium oxide powder (obtained from Aldrich Chemical Company, Inc.), 45 grams of zirconium oxide powder (“DK-2”), 0.6 gram of a dispersing agent (“DURAMAX D-30005”), and 140 grams of distilled water.

FIG. 21 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Example 3 material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 5–15 micrometers in size. Based on powder x-ray diffraction of a portion of Example 3 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline $\text{Dy}_3\text{Al}_5\text{O}_{12}$, and the dark portions $\alpha\text{-Al}_2\text{O}_3$. The shape of ZrO_2 crystallites was not easily discerned on the photomicrograph. The width of the crystals of phases observed in the polished section were up to about 1 micrometer.

Several Example 3 abrasive particles were placed in a platinum crucible and heated to 1000°C . at 50°C./hour , held at 1000°C . for 8 hours (in air), and then cooled to room temperature at about 100°C./hour . The average microhardness of the Example 3 abrasive particles after heating was 15.6 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed for the Example 3 abrasive particles after heating was substantially the same as the microstructure observed before heating.

Example 4

Example 4 fused material and abrasive particles were prepared as described in Comparative Example A, except the polyethylene bottle was charged with 147.9 grams of alumina powder (“APA-0.5”), 137.1 grams of lanthanum oxide powder (obtained from Molycorp, Inc.), 15 grams of zirconium oxide powder (“DK-2”), 0.6 gram of a dispersing agent (“DURAMAX D-30005”), and 145 grams of distilled water.

FIG. 22 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Example 4 material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 5–20 micrometers in size. Based on powder x-ray diffraction of a portion of Example 4 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline LaAlO_3 , the dark portions crystalline $\text{LaAl}_{11}\text{O}_{18}$, and the gray portions crystalline, monoclinic- ZrO_2 . The widths of these phases observed in the polished section were up to about 1.5 micrometer.

Example 5

Example 5 fused material, abrasive particles, and discs were prepared as described in Comparative Example A, except the polyethylene bottle was charged with 109 grams of alumina powder (“APA-0.5”), 101 grams of lanthanum oxide powder (obtained from Molycorp, Inc.), 90 grams of zirconium oxide powder (“DK-2”), 0.6 gram of a dispersing agent (“DURAMAX D-30005”), and 145 grams of distilled water.

FIG. 23 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Example 5 material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. Based on powder x-ray diffraction of a portion of Example 5 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the

photomicrograph were crystalline LaAlO_3 , the dark portions crystalline $\text{LaAl}_{11}\text{O}_{18}$, and the gray portions $\text{La}_2\text{Zr}_2\text{O}_7$. Further, based on powder x-ray diffraction, the material also contained monoclinic and two variants of cubic ZrO_2 . The shape and location of ZrO_2 crystallites was not easily discerned on the photomicrograph.

The average microhardness of Example 5 abrasive particles was determined, as described above in Comparative Example B, to be 12.0 GPa.

Several Example 5 abrasive particles were also placed in a platinum crucible and heated to 1000°C . at 50°C./hour , held at 1000°C . for 8 hours (in air), and then cooled to room temperature at about 100°C./hour . The average microhardness of the Example 5 abrasive particles after heating was 11.8 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed for the Example 5 abrasive particles after heating was substantially the same as the microstructure observed before heating.

The grinding performance of Examples 2, 5, and Comparative Examples E–G coated abrasive discs were evaluated as described above for Comparative Examples A–G. The results are reported in Table 2, below.

TABLE 2

Example	Total cut, g	Final cut, g
Comp. A	404	21
Comp. B	647	51
Comp. C	952	79
2	669	50
5	611	41

Example 6

Example 6 fused material and abrasive particles prepared as described in Example 1, except the polyethylene bottle was charged with 109 grams of alumina powder (“APA-0.5”), 101 grams of lanthanum oxide powder (obtained from Molycorp, Inc.), 9 grams of yttrium oxide powder (obtained from H.C. Starck, Newton, Mass.), 81 grams of zirconium oxide powder (“DK-2”), 0.6 gram of a dispersing agent (“DURAMAX D-30005”), and 145 grams of distilled water.

FIG. 24 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Example 1) of fused Example 6 material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. Based on powder x-ray diffraction of a portion of Example 6 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline LaAlO_3 , the dark portions crystalline $\text{LaAl}_{11}\text{O}_{18}$, and the gray portions cubic ZrO_2 . The shape and location of ZrO_2 crystallites was not easily discerned on the photomicrograph.

Example 7

Example 7 fused material and abrasive particles were prepared as described in Comparative Example A, except the polyethylene bottle was charged with 117 grams of alumina powder (“APA-0.5”), 93 grams of neodymium oxide powder (obtained from Molycorp, Inc.), 90 grams of zirconium oxide powder (“DK-2”), 0.6 gram of a dispersing agent (“DURAMAX D-30005”), and 138 grams of distilled water.

FIG. 25 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Example 7 material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. Based on powder x-ray diffraction of a portion of Example 7 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline NdAlO_3 , and the dark portions crystalline $\text{NdAl}_{11}\text{O}_{18}$. The widths of these phases observed in the polished section were up to about 3 micrometers. Further, based on powder x-ray diffraction, the material also contains two variants of cubic ZrO_2 . The shape and location of ZrO_2 crystallites was not easily discerned on the photomicrograph.

Example 8

Example 8 fused material and abrasive particles were prepared as described in Comparative Example A, except the polyethylene bottle was charged with 106.1 grams of alumina powder ("APA-0.5"), 103.9 grams of cerium (IV) oxide (CeO_2) powder, (obtained from Aldrich Chemical Company, Inc., Milwaukee, Wis.), 90 grams of zirconium oxide powder ("DK-2") 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 139.5 grams of distilled water.

FIG. 26 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Example 8 material. The photomicrograph shows a eutectic-derived microstructure. Based on powder x-ray diffraction of a portion of Example 8, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline CeAlO_3 , the dark portions crystalline $\text{CeAl}_{11}\text{O}_{18}$, and the gray portions $\text{Ce}_2\text{Zr}_2\text{O}_7$. The widths of these phases observed in the polished section were up to about 5 micrometers. Further, based on powder x-ray diffraction, the material also contained monoclinic and two variants of cubic ZrO_2 . The shape and location of ZrO_2 crystallites was not easily discerned on the photomicrograph. Further, large primary crystals (believed to be CeAlO_3 and/or CeO_2) were observed in some areas of the polished cross-section, indicating possible deviation of the composition from an exact eutectic composition toward a CeAlO_3 and/or CeO_2 rich composition.

Comparative Example L

Comparative Example L fused material, abrasive particles, and discs were prepared as described in Comparative Example A, except (a) the polyethylene bottle was charged with 155.6 grams of alumina powder ("APA-0.5"), 144.3 grams of lanthanum oxide powder (obtained from Molycorp, Inc., Brea, Calif.), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 130 grams of distilled water, and (b) the powders were present in amounts to provide 77.5 mole % Al_2O_3 and 22.5 mole % La_2O_3 . The fused material was white-red in color; although some of the abrasive particles were redder than others.

FIG. 27 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Comparative Example L material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 5–30 micrometers in size. Based on powder x-ray diffraction of a portion of Comparative Example B material, and examination of the polished sample using

SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline LaAlO_3 , and the dark portions crystalline $\text{LaAl}_{11}\text{O}_{18}$. The widths of these phases observed in the polished section were up to about 0.5 micrometer. Further, large primary crystals (believed to be LaAlO_3), present in the form of dendrites, were observed in some areas of the polished cross-section, indicating possible deviation of the composition from an exact eutectic composition toward a La_2O_3 rich composition.

The grinding performance of Comparative Examples E–G and L coated abrasive discs were evaluated as described above for Comparative Examples A–G. The results are reported in Table 3, below.

TABLE 3

Example	Total cut, g	Final cut, g
Comp. E	404	21
Comp. F	647	51
Comp. G	952	79
Comp. L	690	52

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

What is claimed is:

1. Fused, crystalline eutectic material comprising eutectic of at least:

(a) crystalline ZrO_2 and

(b) at least two of:

(i) crystalline Al_2O_3 ,

(ii) first crystalline complex Al_2O_3 .rare earth oxide, or

(iii) second, different, crystalline complex Al_2O_3 .rare earth oxide.

2. The fused, crystalline eutectic material according to claim 1 comprising, on a theoretical oxide basis, at least 40 percent by weight Al_2O_3 , based on the total metal oxide content of said eutectic material.

3. The fused, crystalline eutectic material according to claim 2, wherein said rare earth oxide is selected, on a theoretical oxide basis, from the group consisting of CeO_2 , Dy_2O_3 , Er_2O_3 , Eu_2O_3 , Gd_2O_3 , La_2O_3 , Nd_2O_3 , Pr_6O_{11} , Sm_2O_3 , Yb_2O_3 , and combinations thereof.

4. The fused, crystalline eutectic material according to claim 2 comprising colonies of said eutectic, and wherein said colonies have an average size of less than 100 micrometers.

5. The fused, crystalline eutectic material according to claim 4, wherein said colonies have an average size of less than 50 micrometers.

6. The fused, crystalline eutectic material according to claim 2 comprising colonies of said eutectic, and wherein crystals making up said colonies are, on average, up to 10 micrometers in size.

7. The fused, crystalline eutectic material according to claim 6, wherein said crystals are, on average, up to 1 micrometer in size.

8. The fused, crystalline eutectic material according to claim 2, wherein said eutectic is selected from the group consisting of Al_2O_3 — $\text{Dy}_3\text{Al}_5\text{O}_{12}$ — ZrO_2 eutectic, Al_2O_3 — $\text{Er}_3\text{Al}_5\text{O}_{12}$ — ZrO_2 eutectic, Al_2O_3 — GdAlO_3 — ZrO_2 , eutectic and Al_2O_3 — $\text{Yb}_3\text{Al}_5\text{O}_{12}$ — ZrO_2 eutectic.

9. The fused, crystalline eutectic material according to claim 8 further comprising primary crystals of Al_2O_3 .

10. The fused, crystalline eutectic material according to claim 2, wherein said eutectic is selected from the group consisting of $\text{CeAlO}_3\text{—CeAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, $\text{EuAlO}_3\text{—EuAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, $\text{LaAlO}_3\text{—LaAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, $\text{NdAlO}_3\text{—NdAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, $\text{PrAlO}_3\text{—PrAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, and $\text{SmAlO}_3\text{—SmAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic.

11. The fused, crystalline eutectic material according to claim 2, wherein said eutectic is $\text{LaAlO}_3\text{—LaAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic.

12. The fused, crystalline eutectic material according to claim 2 further comprising at least one of crystalline Y_2O_3 or crystalline complex $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$.

13. The fused, crystalline eutectic material according to claim 2 further comprising at least one of crystalline BaO , CaO , Cr_2O_3 , CoO , Fe_2O_3 , HfO_2 , Li_2O , MgO , MnO , NiO , SiO_2 , TiO_2 , Na_2O , SrO , Sc_2O_3 , V_2O_3 , ZnO , or complex $\text{Al}_2\text{O}_3\cdot\text{metal oxide}$ thereof.

14. The fused, crystalline eutectic material according to claim 2 having an average microhardness of at least 13 GPa.

15. The fused, crystalline material according to claim 3, wherein said complex $\text{Al}_2\text{O}_3\cdot\text{REO}$ further comprises cations selected from the group consisting of Cr , Ti , Sc , Fe , Mg , Ca , Si , Co , Y , Mn , V , Ni , Cu , Sr , and combinations thereof.

16. Fused, crystalline eutectic material comprising eutectic of at least:

- (a) crystalline ZrO_2 and
- (b) at least two of:
 - (i) crystalline Al_2O_3 ,
 - (ii) first crystalline complex $\text{Al}_2\text{O}_3\cdot\text{rare earth oxide}$, or
 - (iii) second different, crystalline complex $\text{Al}_2\text{O}_3\cdot\text{rare earth oxide}$,

wherein the fused, crystalline eutectic material comprises, on a theoretical oxide basis, at least 40 percent by weight Al_2O_3 , based on the total metal oxide content of said eutectic material, wherein said rare earth oxide is selected, on a theoretical oxide basis, from the group consisting of CeO_2 , Dy_2O_3 , Er_2O_3 , Eu_2O_3 , Gd_2O_3 , La_2O_3 , Nd_2O_3 , Pr_6O_{11} , Sm_2O_3 , Yb_2O_3 , and combinations thereof, and wherein a portion of said complex $\text{Al}_2\text{O}_3\cdot\text{rare earth oxide}$ Al cations are substituted with at least one cation of an element selected from the group consisting of: Cr , Ti , Sc , Fe , Mg , Ca , Si , Co , and combinations thereof.

17. Fused, crystalline eutectic material comprising eutectic of at least:

- (a) crystalline ZrO_2 and
- (b) at least two of:
 - (i) crystalline Al_2O_3 ,
 - (ii) first crystalline complex $\text{Al}_2\text{O}_3\cdot\text{rare earth oxide}$, or
 - (iii) second, different, crystalline complex $\text{Al}_2\text{O}_3\cdot\text{rare earth oxide}$,

wherein the fused, crystalline eutectic material comprises, on a theoretical oxide basis, at least 40 percent by weight Al_2O_3 , based on the total metal oxide content of said eutectic material, wherein said rare earth oxide is selected, on a theoretical oxide basis, from the group consisting of CeO_2 , Dy_2O_3 , Er_2O_3 , Eu_2O_3 , Gd_2O_3 , La_2O_3 , Nd_2O_3 , Pr_6O_{11} , Sm_2O_3 , Yb_2O_3 , and combinations thereof, and wherein a portion of said complex rare earth oxide rare earth cations are substituted with at least one cation of an element selected from the group consisting of: Ce , Dy , Er , Eu , Gd , Ho , La , Lu , Nd , Pr , Sm , Th , Tm , Yb , and combinations thereof.

18. Fused, crystalline eutectic material comprising eutectic of at least:

- (a) crystalline ZrO_2 and
- (b) at least two of:
 - (i) crystalline Al_2O_3 ,
 - (ii) first crystalline complex $\text{Al}_2\text{O}_3\cdot\text{rare earth oxide}$, or
 - (iii) second, different, crystalline complex $\text{Al}_2\text{O}_3\cdot\text{rare earth oxide}$,

wherein the fused, crystalline eutectic material comprises, on a theoretical oxide basis, at least 40 percent by weight Al_2O_3 , based on the total metal oxide content of said eutectic material, wherein said rare earth oxide is selected, on a theoretical oxide basis, from the group consisting of CeO_2 , Dy_2O_3 , Er_2O_3 , Eu_2O_3 , Gd_2O_3 , La_2O_3 , Nd_2O_3 , Pr_6O_{11} , Yb_2O_3 , and combinations thereof, and wherein a portion of said complex $\text{Al}_2\text{O}_3\cdot\text{rare earth oxide}$ rare earth cations are substituted with at least one cation of an element selected from the group consisting of: Fe , Ti , Mn , V , Cr , Co , Ni , Cu , Mg , Ca , Sr , and combinations thereof.

19. The fused, crystalline eutectic material according to claim 1, wherein said eutectic is selected from the group consisting of $\text{Al}_2\text{O}_3\text{—Dy}_3\text{Al}_5\text{O}_{12}\text{—ZrO}_2$ eutectic, $\text{Al}_2\text{O}_3\text{—Er}_3\text{Al}_5\text{O}_{12}\text{—ZrO}_2$ eutectic, $\text{Al}_2\text{O}_3\text{—GdAlO}_3\text{—ZrO}_2$ eutectic, and $\text{Yb}_3\text{Al}_5\text{O}_{12}\text{—ZrO}_2$ eutectic, wherein said fused, crystalline eutectic material further comprises primary crystals of a metal oxide corresponding to said eutectic, and wherein said primary crystals are selected from the group consisting of $\text{Dy}_3\text{Al}_5\text{O}_{12}$, $\text{Er}_3\text{Al}_5\text{O}_{12}$, GdAlO_3 , and $\text{Yb}_3\text{Al}_5\text{O}_{12}$.

20. The fused, crystalline eutectic material according to claim 1, wherein said eutectic is selected from the group consisting of $\text{CeAlO}_3\text{—CeAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, $\text{EuAlO}_3\text{—EuAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, $\text{LaAlO}_3\text{—LaAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, $\text{NdAlO}_3\text{—ZrO}_2$ eutectic, $\text{PrAlO}_3\text{—PrAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, and $\text{SmAlO}_3\text{—SmAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, wherein said fused, crystalline eutectic material further comprises primary crystals of a metal oxide corresponding to said eutectic, and wherein said primary crystals are selected from the group consisting of CeAlO_3 , EuAlO_3 , LaAlO_3 , NdAlO_3 , PrAlO_3 , and SmAlO_3 .

21. The fused, crystalline eutectic material according to claim 1, wherein said eutectic is selected from the group consisting of $\text{CeAlO}_3\text{—CeAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, $\text{EuAlO}_3\text{—EuAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, $\text{LaAlO}_3\text{—LaAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, $\text{NdAlO}_3\text{—NdAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, $\text{PrAlO}_3\text{—PrAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, and $\text{SmAlO}_3\text{—SmAl}_{11}\text{O}_{18}\text{—ZrO}_2$ eutectic, wherein said fused, crystalline eutectic material further comprises primary crystals of a metal oxide corresponding to said eutectic, and wherein said primary crystals are selected from the group consisting of $\text{CeAl}_{11}\text{O}_{18}$, $\text{EuAl}_{11}\text{O}_{18}$, $\text{LaAl}_{11}\text{O}_{18}$, $\text{NdAl}_{11}\text{O}_{18}$, $\text{PrAl}_{11}\text{O}_{18}$, and $\text{SmAl}_{11}\text{O}_{18}$.

22. The fused, crystalline eutectic material according to claim 1, wherein said eutectic is eutectic of at least (a) crystalline ZrO_2 , (b) crystalline Al_2O_3 , and (c) crystalline complex $\text{Al}_2\text{O}_3\cdot\text{rare earth oxide}$.

23. The fused, crystalline eutectic material according to claim 1, wherein said eutectic is eutectic of at least (a) crystalline ZrO_2 , (b) first crystalline complex $\text{Al}_2\text{O}_3\cdot\text{rare earth oxide}$, and (c) second, different, crystalline complex $\text{Al}_2\text{O}_3\cdot\text{rare earth oxide}$.

24. Fused, crystalline eutectic material comprising eutectic of at least:

- (a) crystalline complex $\text{Al}_2\text{O}_3\cdot\text{rare earth oxide}$ and
- (b) crystalline ZrO_2 .

25. The fused, crystalline eutectic material according to claim 24 wherein at least a majority by weight of said crystalline ZrO_2 is cubic ZrO_2 .

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,582,488 B1
DATED : June 24, 2003
INVENTOR(S) : Rosenflanz, Anatoly Z.

Page 1 of 5

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page,

Item [54], Title, delete "**ZRO₂**" and insert in place thereof -- **ZrO₂** --.

Item [56], **References Cited**, U.S. PATENT DOCUMENTS,

"4,070,796 A 1/1978 Scott" should read
-- 4,070,796 A 1/1978 Scott et al. --.
"4,439,845 A 3/1984 Geohegan, Jr. et al." should read
-- 4,439,845 A Richmond. --.
"Re31,725 B 11/1984 Walker et al." should read
-- Re31,725 B 1/1984 Walker et al. --.
"4,751,137 A 6/1988 halg et al." should read
-- 4,751,137 A 6/1988 Tumey et al. --.
"4,800,685 A 1/1989 Haynes, Jr." should read
-- 4,800,685 A 1/1989 Haynes, Jr. et al. --.
"4,997,461 A 3/1991 Markhof-Matheny et al." should read
-- 4,997,461 A 3/1991 Markhoff Matheny et al. --.
Insert -- 5,027,886 A 6/2003 Rosenflanz et. al. --.
"5,038,453 A 8/1991 Kurita et al." should read
-- 5,038,453 A 8/1991 Narayannan et al. --.
"5,110,332 A 5/1992 Isaksson" should read
-- 5,110,332 A Narayannan et al. --.
"5,118,326 A 6/1992 Lee et al." should read
-- 5,118,326 A 6/1992 Sheldon et al. --.
"5,131,926 A 7/1992 Rostoker et al." should read
-- 5,131,926 A 7/1992 --.
"Sheldon, et al. 5,429,647 A 7/1995 Laramie" should read
-- 5,429,647 A 7/1995 Larmie --.
"5,738,696 A 4/1998 Wu" should read
-- 5,738,696 A 4/1998 Wu et al. --.
"5,863,308 A 1/1999 Qi et al. " should read
-- 5,863,308 A 1/1999 Qi --.

OTHER PUBLICATIONS,

"A ductile" reference, delete "eutetic" preceding "composite" and insert in place thereof -- eutectic --.

"Metastable" reference, delete "Lakiz" preceding "and " and insert in place thereof -- Lakiza --.

"Figs. 5042" reference, delete "1 43," preceding "220," and insert in place thereof -- 143 --.

"Abstract for "Kinetics"" reference, delete "sintenic" preceding "of" and insert in place thereof -- sintering --.

"Dow Jones" 4th and 6th reference, delete "/" following "story" and insert in place thereof -- . -- in all instances.

"Dow Jones" 7th reference, delete "," following "story" and insert in place thereof -- . --; and delete "Earth" following "Rare" and insert in place thereof -- Earths --.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,582,488 B1
DATED : June 24, 2003
INVENTOR(S) : Rosenflanz, Anatoly Z.

Page 2 of 5

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 1,

Line 1, delete "ZRO₂" and insert in place thereof -- Z_rO₂ --.

Line 8, insert -- rare earth oxide -- following "YI₂O₃".

Line 8, insert -- -ZrO₂ -- following "oxide".

Line 45, delete "O₃" and insert in place thereof -- O₃ --.

Line 59, insert -- of -- following "content".

Column 2,

Line 7, delete "Y₃" and insert in place thereof -- Y₂ --.

Line 29, delete "DRAWING" and insert in place thereof -- DRAWINGS --.

Line 52 and 53, delete "sections" and insert in place thereof -- section --.

Line 55, delete "FIG." and insert in place thereof -- FIGS. --.

Column 3,

Line 2, insert -- to -- following "used".

Line 8, delete "oxides" and insert in place thereof -- oxide --.

Line 9, delete "homogenous" and insert in place thereof -- homogeneous --.

Line 24, insert -- Al₂O₃ -- following "an".

Line 39, delete "and" following "and/or".

Line 40, delete "," following "material".

Column 4,

Line 4, insert --)- -- following "respectively".

Line 36, insert -- are -- following "that".

Lines 45 and 57, delete "with in" and insert in place thereof -- within --.

Column 5,

Line 9, delete "-" following "REO".

Line 14, insert -- , -- following "Al₂O₃".

Line 19, delete "oxide" and insert in place thereof -- oxides --.

Column 6,

Line 34, insert -- having -- following "particle".

Column 7,

Lines 15 and 46, delete "comprise" and insert in place thereof -- comprises --.

Line 39, delete "form" and insert in place thereof -- forms --.

Line 39, insert -- the -- following "of".

Line 49, delete "metals" and insert in place thereof -- metal --.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,582,488 B1
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INVENTOR(S) : Rosenflanz, Anatoly Z.

Page 3 of 5

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 8,

Line 12, insert -- to -- following "up".

Column 9,

Line 22, insert -- a -- following "high".

Line 29, delete "homogenous" and insert in place thereof -- homogeneous --.

Column 10,

Line 26, insert -- material -- following "fused".

Line 41, delete "technique" and insert -- techniques --.

Line 47, delete "increase" and insert in place thereof -- increases --.

Line 59, delete "Re" preceding "3,781,172".

Line 60, delete "RE" preceding "4,070,796".

Line 60, delete "RE" preceding "4,194,887".

Line 61, delete "RE" preceding "4,415,510".

Line 62, delete "RE" preceding "4,439,845".

Line 62, delete "RE" preceding "5,027,886".

Line 63, delete "RE" preceding "5,143,522".

Column 11,

Line 42, insert -- from -- following "range".

Column 12,

Line 10, delete "disclosure" and insert in place thereof -- disclosures --.

Line 12, delete "09/496,422," and insert in place thereof -- 09/496,442, --.

Line 16, delete "disclosure" and insert in place thereof -- disclosures --.

Line 23, insert -- of -- preceding "adjacent".

Line 25, delete "(- shaped phase)" and insert in place thereof -- -shaped phase --.

Line 38, delete "boundary" and insert in place thereof -- boundaries --.

Lines 40 and 65, delete "material" and insert in place thereof -- materials --.

Column 13,

Lines 20, 33, 38, 44, 46 and 47, delete "material" and insert in place thereof -- materials --.

Line 46, delete "result" and insert in place thereof -- results --.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,582,488 B1
DATED : June 24, 2003
INVENTOR(S) : Rosenflanz, Anatoly Z.

Page 4 of 5

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 14,

Line 26, delete "5, 609,706" and insert in place thereof -- 5,609,706 --.

Line 30, delete "Hagnes et al" and insert in place thereof -- Haynes Jr. et al. --.

Line 34, delete "Giles et al" and insert in place thereof -- Giles Jr. et al. --.

Line 37, insert -- U.S. Pat. No. -- preceding "5,738,696".

Line 39, delete "disclosure" and insert in place thereof -- disclosures --.

Line 64, delete "Dear" and insert in place thereof -- Deer --.

Column 15,

Line 14, insert -- a -- preceding "rate".

Line 16, delete "power" following "furnace".

Line 17, insert -- was -- preceding "allowed".

Column 17,

Line 44, delete "flit" and insert in place thereof -- frit --.

Line 48, insert -- . -- following "No".

Column 18,

Line 9, delete "were" and insert in place thereof -- was --.

Column 21,

Lines 13, 21 and 22, delete "example" and insert in place thereof -- Example --.

Line 16, delete "Triebacher" and insert in place thereof -- Treibacher --.

Lines 41 and 42, insert -- of -- preceding "a".

Line 54, delete "111" and insert in place thereof -- 11 \bar{I} --.

Column 22,

Lines 8 and 28, insert -- of -- preceding "a".

Line 57, delete "was" and insert in place thereof -- were --.

Column 23,

Line 3, delete "workpiece" and insert in place thereof -- workpieces --.

Line 7, insert -- the -- following "at".

Column 25,

Line 20, delete "111" and insert in place thereof -- 11 \bar{I} --.

Line 37, delete "was" and insert in place thereof -- were --.

Line 56, delete "Examples" and insert in place thereof -- Example --.

Line 57, delete "Example k I" and insert in place thereof -- Example k --.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 6,582,488 B1
DATED : June 24, 2003
INVENTOR(S) : Rosenflanz, Anatoly Z.

Page 5 of 5

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 28,

Lines 23 and 24, delete "Comparative Examples E-G" and insert in place thereof -- Comparative Examples A-C --.

Line 38, insert -- were -- preceding "prepared".

Column 31,

Line 35, insert -- , -- following "second".

Line 45, delete "clement" and insert in place thereof -- element --.

Column 32,

Line 14, insert -- Sm_2O_3 , -- following " Pr_6O_{11} ".

Line 23, insert -- Al_2O_3 -- following "and".

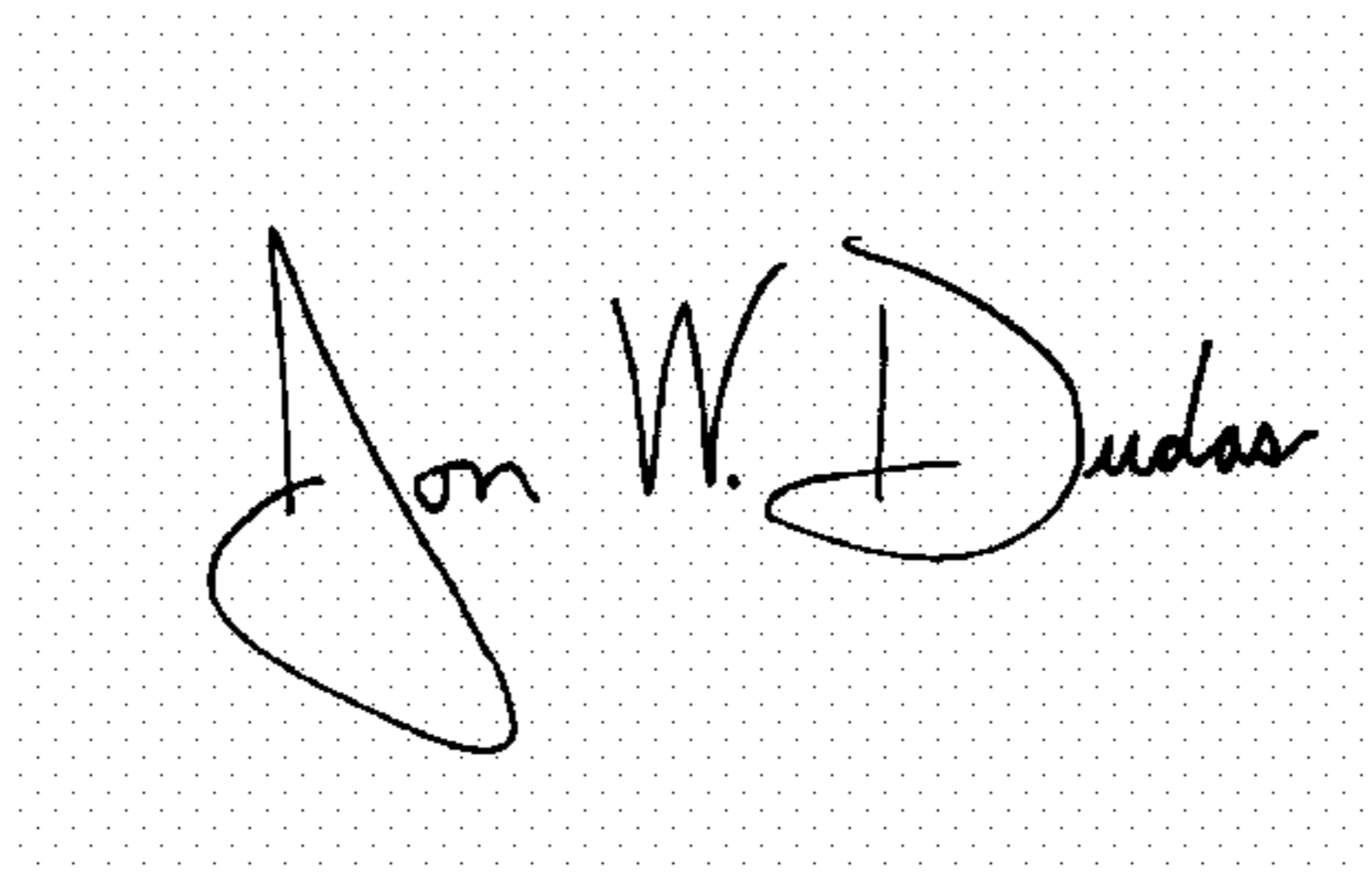
Line 31, delete "ZrO2" and insert in place thereof -- ZrO_2 --.

Line 33, insert -- $\text{NdAl}_{11}\text{O}_{18}$ -- preceding " ZrO_2 ".

Line 50, " $\text{Ce Al}_1\text{O}_{18}$ " should be -- $\text{Ce Al}_{11}\text{O}_{18}$ --.

Signed and Sealed this

Twenty-third Day of August, 2005

A handwritten signature in black ink on a dotted background. The signature reads "Jon W. Dudas" in a cursive style.

JON W. DUDAS

Director of the United States Patent and Trademark Office